Russian Chemical Reviews **64**(2) 99–124 (1995)
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UDC 547.714.04

1,6-Electrocyclic reactions

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Abstract. New data on the thermal and photochemical reactions between hexa-1,3,5-trienes and cyclohexadienes as well as their heteroanalogues are surveyed. The bibliography includes 283 references.

I. Introduction

Electrocyclic reactions include the rearrangement of linear alkenes with a conjugated system of π-bonds accompanied by the formation of a new σ-bond and ring closure as well as the reverse rearrangements involving the dissociation of a σ-bond in a cyclic unsaturated compound and the formation of compounds with a conjugated system of π-bonds. The study of such reactions began as early as the beginning of this century.[1–3] Among them, an important place is occupied by 1,6-electrocyclic reactions (1,6-ER), which are six-electron electrocyclic processes. These include the cyclisation reactions of hexatriene, its derivatives, and its heteroanalogues as well as the ring opening in cyclohexadiene. The cyclisation of hexatriene to cyclohexadiene was first achieved in 1964.

After the theory of pericyclic processes had been developed,[1–3] these studies began to develop vigorously. The details of the mechanism of the cyclisation of hexatriene were investigated and numerous theoretical studies of 1,6-electrocyclic reactions involving quantum-chemical calculations were published.

More than 800 communications on 1,6-ER have now been published and half of them appeared during the last decade. They include a series of reviews devoted to individual questions of 1,6-ER or problems associated with these reactions. Marvell's book,[4] in which the literature on thermal ER published up to 1979 is surveyed, appeared in 1980. Unfortunately it does not include photochemical electrocyclic reactions, which are of enormous interest for the understanding of the characteristic features of electrocyclic processes.

Among the latest advances in this field, mention should be made of the development of a new approach to the synthesis of cyclic systems: electrocyclic and other pericyclic reactions, occurring successively, making it possible to obtain a whole series of highly effective antibiotics; a series of investigations demonstrating that the 1,6-ER of trienes is one of the stages in the mechanism of the action of a series of highly active antitumour preparations; the development of new photochromic systems on the basis of the ER of hexatriene hetero-analogues.

The present review deals with the continuation of the present author's investigations[5,6] and contains data on thermal and photochemical 1,6-ER.

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Received 7 June 1994
Uspekhi Khimii **64**(2) 107–132 (1995); translated by A K Grzybowski

II. Theoretical investigations

There have been relatively few studies on the cyclisation of hexa-1,3,5-trienes and their hetero-analogues. Lewis and Steiner[7] calculated the activation parameters for this reaction by the method of Evans and Polanyi.[8] Marvell[9] used a modified Hendrickson method for the determination of the influence of substituents on the rate of reaction.

Attempts have been made to predict and explain the reactivity of hexa-1,3,5-trienes by Hückel's method[10] and by various semiempirical methods: PPP,[11] MINDO/2,[12] MINDO/3,[13–16] MNDO,[17] CNDO/2S,[18] and AM1,[19] as well as ab initio methods with the 3-21G, 6-31G, and 6-31G + MP2 basis sets.[20]

The activation energies for the thermal cyclisation of hexa-1,3,5-triene, determined by the MINDO/2 and MINDO/3 methods, are 24.6 kcal mol^{-1},[12] and 33.2 kcal mol^{-1},[16] respectively, which are close to the experimental value (29.4 kcal mol^{-1}).[1–3]

It has been shown that true transition states (TS) correspond to both the 'allowed' and 'forbidden' paths in the thermal reaction.[16] However, the transition state corresponding to the conrotatory path is asymmetric.[16] The authors[16] showed that, when the hydrogen atoms at the C(2) and C(5) atoms of the hexatriene system are located on one side of the molecular plane, a disrotatory transition state is indicated, while their location on each side of the molecular plane is evidence for a conrotatory transition state.[16]

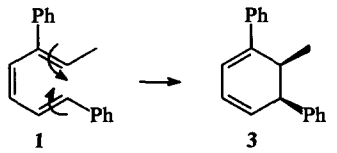
Gatti et al.[21] used the topological theory of molecular structures to investigate the reactions of cyclic systems. Baldwin et al.[22] calculated the kinetic isotope effect in the cyclisation of hexa-1,3,5-triene with the aid of semiempirical calculations in terms of the 6-31G basis set. The values obtained proved to be close to the experimental data.[22]

Bock et al.[23] presented data on the interconversion of benzene oxide and oxepine—the oxa-analogues of cyclohexadiene and hexa-1,3,5-triene. The calculations were performed by the AM1 and *ab initio methods in terms of the* 6-21G, 6-31G, and 6-31G + MP3 basis sets.[23] The authors showed that the best agreement between the calculated and experimental data is attained when third-order perturbation theory is used to perform the calculations.[23]

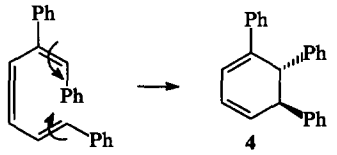
Calculations have been performed for the photochemical isomerisation of cyclohexadiene to hexatriene by means of the MRDCI method.[24]

III. Stereochemical characteristics of 1,6-electrocyclic reactions

According to the rules for the conservation of orbital symmetry, the cyclisation of hexa-1,3,5-trienes should be disrotatory in the ground state and conrotatory in the excited state.[1-3] This conclusion has been confirmed by numerous theoretical and experimental studies.[1-3] According to MINDO/3 calculations, the disrotatory path to the cyclisation of hexa-1,3,5-triene is preferred to the conrotatory path to the extent of 14.5 kcal mol^{-1}.[13] Padwa et al.[25] showed that, on heating in toluene, the trienes **1** and **2** undergo disrotatory cyclisation to the cyclohexadienes **3** and **4**. The products of the conrotatory cyclisation were not detected under these conditions.

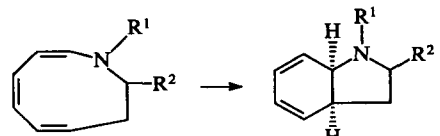


1 **3**



2 **4**

In a study of the thermolysis of *cis*-5,6-dimethylcyclohexadiene and 1-phenylhepta-1,3,5-triene, it was shown that the yield of the products of the conrotatory cyclisation is less than 0.5%.[4] The cyclic trienes **5** give rise to the bicyclic compounds **6** with a *cis*-disposition of the substituents at the bridging carbon atoms, which is also evidence for a disrotatory process.[26,27]



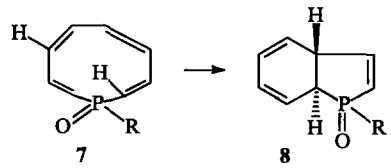
5a,b **6a,b**

R^1 = CO_2Me, R^2 = CH_2Ph (**a**);

R^1 = Ph, R^2 = CH_2Ph (**b**).

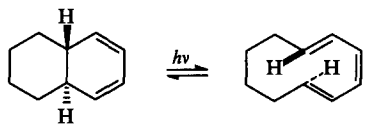
However, it is essential to note that experiments indicating disrotatory cyclisation of compound **5** are not very convincing, since the bicyclic compounds **6** are formed from initial compounds having a specific geometry.

The experiment of Quin et al.[28] is especially interesting in this connection. They showed that the tetraene **7**, the geometry of which should promote conrotatory cyclisation, actually cyclises to the bicyclic product **8** with a *trans*-disposition of the hydrogen atoms at the bridging carbon atoms.[28]

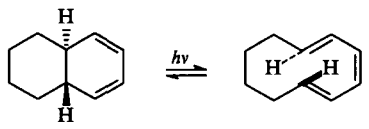


7 **8**

The most striking examples confirming the conrotatory mechanism of the photocyclisation of the cycloala-1,3,5-trienes[21] is provided by experiments with the optically active dienes **9**. When the dienes **9** are irradiated, the ring opens with retention of the chirality and the photocyclisation of the resulting trienes **10** leads to the exclusive formation of the initial enantiomers.[29]



(−)-**9** (+)-**10**



(+)-**9** (−)-**10**

IV. Thermodynamic and kinetic investigations

The energy of activation for the formation of cyclohexa-1,3-diene from *cis*-hexa-1,3,5-triene is 29 kcal mol^{-1}.[4] Thermochemical determination of the heats of formation of cyclohexa-1,3-diene and *cis*-hexa-1,3,5-triene (25.38 and 40.58 kcal mol^{-1}) has made it possible to calculate the heat of formation of the transition state in this reaction (69.6 kcal mol^{-1}) and the energy of activation for the opening of the cyclohexa-1,3-diene ring (44.2 kcal mol^{-1}).[4]

The difference between the allowed disrotatory and forbidden conrotatory paths is 5 kcal mol^{-1} according to the authors' estimate[4] and 14.5 kcal mol^{-1} according to calculations by the MINDO/3 method.[13]

Kinetic studies have been carried out on the cyclisation of acyclic[4] and cyclic[4,29-39] hexatrienes as well as their heteroanalogues.[37-39]

Kinetic data have been published recently for photochemical 1,6-ER.[40,41] The most complete set of activation parameters for 1,6-ER has been presented in a monograph.[4] Treatment of the experimental data with the aid of CAMEO† programs permitted the following generalisations:[42]

1. When the triene system is incorporated in a ring, the activation energy diminishes by 2 kcal mol^{-1}.

2. *cis*-Substituents in the terminal positions of the conjugated systems increase the corresponding activation energy, apparently as a result of the deviation from planarity by 2 kcal mol^{-1}.

3. The activation energy for the cyclisation of trienes in which the terminal atom is part of a cumulene system is reduced by 10 kcal mol^{-1}.

4. The activation energy for the ER involving cyclic π-systems should be apprreciably lower than in the case of acyclic analogues. If the triene is part of a ring in which the number of atoms is more than six, then E_a diminishes by 10 kcal mol^{-1}.

5. If the cyclisation of trienes results in the formation of a three- or four-membered ring, then E_a increases by 10 kcal mol^{-1}.

6. If the cyclisation disturbs or generates aromaticity, E_a increases or diminishes by 8 kcal mol^{-1}.

† CAMEO = Computer-assisted mechanistic evaluation of organic reactions.

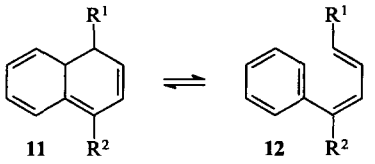
Unfortunately, the authors [42] did not include all the literature data then available in the information which they interpreted. Because of this, the well established fact that the cyclisation of 1,3,5-trienes is accelerated by the introduction of substituents in the 2- or 5-position remained outside the limits of their assessment. [4] Marvell [4] explained this effect by the decrease in the steric interactions of the substituent with the triene system in the transition state having the *cis*-(*Z*)-*cis*-conformation, compared with the initial compound which exists predominantly in the *cis*-(*Z*)-*trans*-form. [4]

V. Thermal processes

1. Reactions of acyclic compounds

It has been already noted that cyclohexadienes are more stable than hexatrienes, but if the opening of the cyclohexadiene ring results in the formation of an aromatic ring then this may alter and facilitate the process.

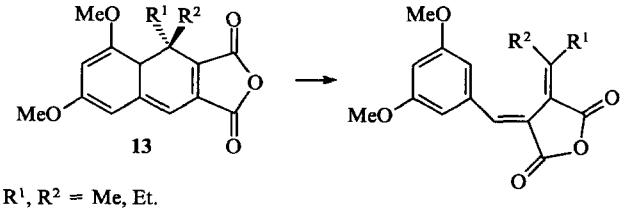
With the aid of deuterium labels, Lamberts and coworkers [43–45] showed that the flash thermolysis of the dihydronaphthalenes **11** results in the opening of the cyclohexa-1,3-diene ring and the formation of the butadiene derivatives **12**. The authors [45] established that only compounds where the recyclisation leads to the formation of an aromatic ring enter into the reaction.



11 **12**

R^1, R^2 = H, Ph, 4-MeC_6H_4.

The formation of an aromatic ring may be the cause of the ready opening of the cyclohexadiene ring in the tricyclic compound **13**. The reaction takes place even at 28 °C. [46]

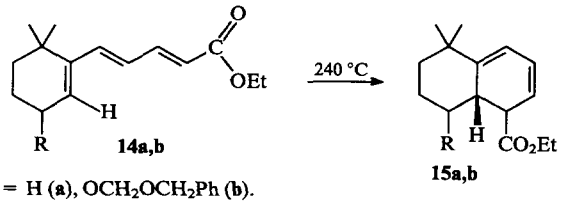


13

R^1, R^2 = Me, Et.

Trienes cyclise to hexadienes as a rule at elevated temperatures. [4] This is associated with the high energy barrier in the isomeric interconversions between the *cis*- and *trans*-isomeric forms of hexatriene. Thus compounds **14** cyclise only at temperatures above 240 °C. [47]

It has been shown [47] that the cyclisation of compound **14b** results in the formation of only one diastereoisomer **15b**, which indicates an effective stereocontrol by the OCH_2OCH_2Ph group. This implies the possibility of carrying out asymmetric syntheses of compounds **15**, which are the starting materials for the synthesis of forskolin — an oxygen-containing diterpene exhibiting a broad spectrum of physiological activity. [47]



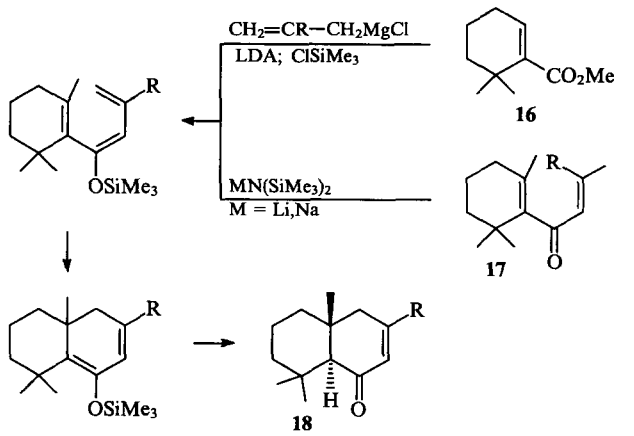
14a,b **15a,b**

R = H (**a**), OCH_2OCH_2Ph (**b**).

The introduction of the electron-accepting carbamoyl groups in the 2- and 5-positions in the hexatriene system greatly facilitates the cyclisation and the process takes place smoothly already at 200 °C. [4]

The photochemical reaction involving the opening of the cyclohexadiene ring is frequently employed to obtain trienes with a *cis*-(*Z*)-*cis*-configuration. [4]

An interesting method for the generation of trienes by the Grignard reaction from methyl β-cyclogeranate **16** or by the deprotonation of the enone **17** has been described. [48]



16 **17** **18**

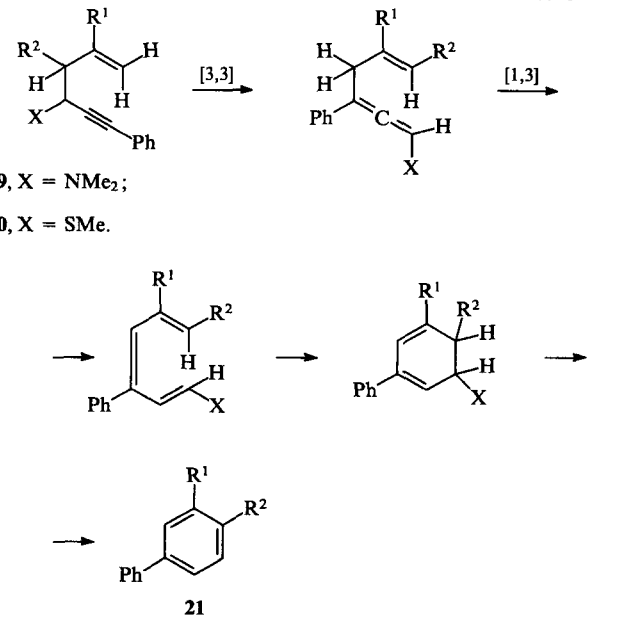
R = H, Me;

LDA = $(Pr^i)_2NLi$.

This process and the subsequent electrocyclisation constitute a new method of synthesis of the cyclic enone **18**.

It has been shown [49] that the ynamine **19** and the thioether **20** can serve as sources of hexatrienes. Moderate thermolysis of these compounds leads to the formation of the benzene derivative **21** (Scheme 1).

Scheme 1



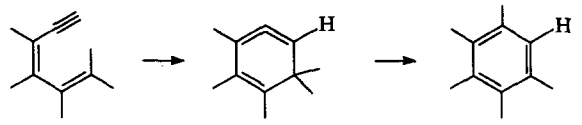
19, X = NMe_2;

20, X = SMe.

21

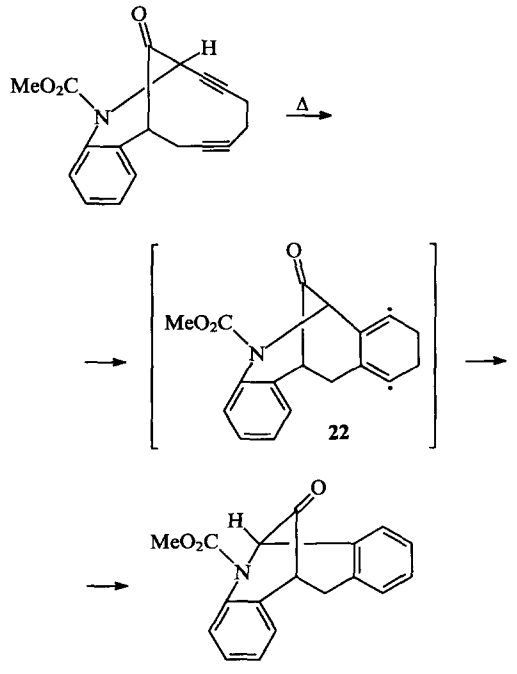
The substitution of one or both terminal double bonds in the hexa-1,3,5-triene by triple bonds does not prevent the cyclisation. [4]

The thermal cyclisation is carried out at elevated temperatures (~300 °C), but in the presence of strong bases it is possible to carry out this reaction at 80 °C. The rate-limiting stage is apparently the migration of hydrogen, but it has been shown that other groups can also migrate. [50]

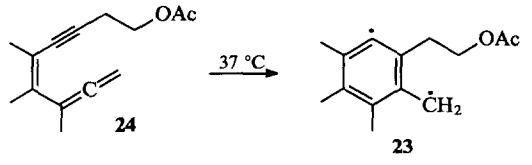


Systems of conjugated multiple bonds enter into the composition of the molecules of daunomycin, neocarzinostatin, and esperamicin–antibiotics with a high antitumour activity.[51–55]

It has been suggested[53,54] that the mechanism of the biological action of these compounds is associated with the formation of the tricyclic biradical **22**, which can abstract hydrogen from DNA and thus damage its helix. It has been demonstrated by kinetic investigations that the rate of cyclisation of such systems increases with decrease in the distance between the terminal atoms of the conjugated π-system.[51,52]

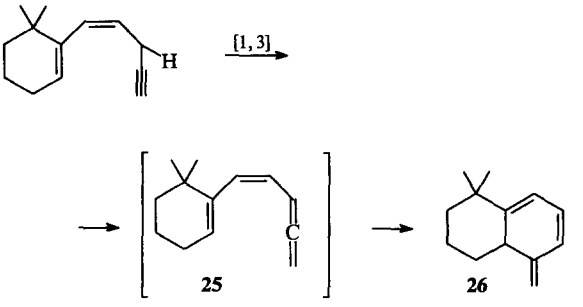


Ethynyldienes in which the terminal π-bond is part of an allene group are also biologically important. They are part of the molecules of antibiotics of the enediyne series.[56,57] It has been suggested that Bergman type electrocyclisation of these compounds, which leads to the biradical **23**, plays an important role in the cleavage of the DNA helix by antibiotics of the enediyne series.[56]



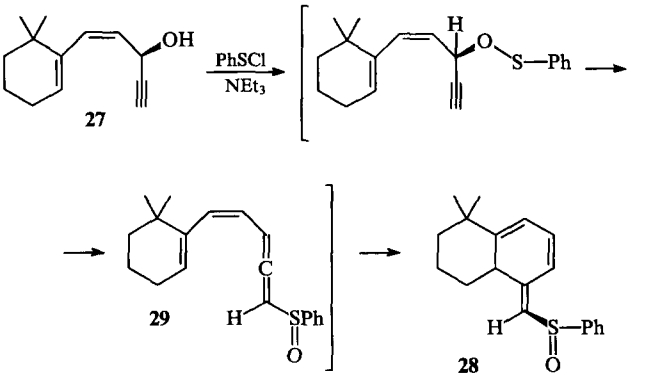
The activation energies E_a have been determined[56] for the cyclisation of a series of type **24** compounds and it has been shown that steric factors affect its rate to a greater extent than electronic factors.

The trienes **25**, in which one π-bond enters into the composition of an allene group, are unstable and are readily transformed into compounds **26**.[58]

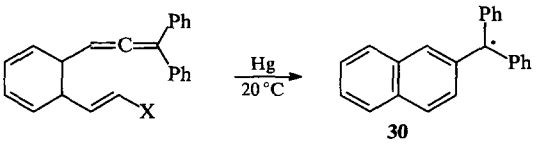


It has been demonstrated[58] that the electrocyclic reaction takes place with a lower value of E_a than the 1,3-sigmatropic shift of hydrogen.

The interaction of the optically active *cis*-propargyl alcohol **27** with benzenesulfenyl chloride leads exclusively to the diastereoisomer **28**.[58] The authors[58] claim that this reaction is a stereospecific tandem centre–axis–centre transfer and that the cyclisation of compound **29** takes place via a disrotatory mechanism.



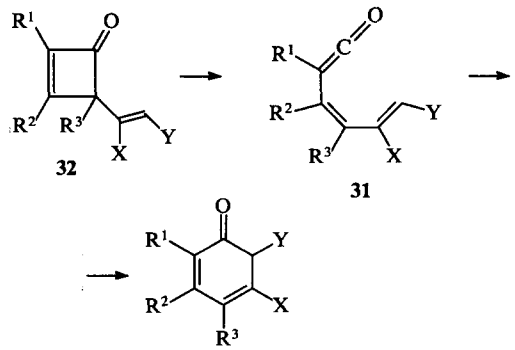
It is of interest to note that the cyclisation of butadienylallenes in the presence of elemental mercury leads to the stable triarylmethyl radical **30**.



X = Cl, Br.

When one double bond of the 1,3,5-triene system is part of a ketene group, the rate of electrocyclisation increases greatly.[4]

The butadienylketenes **31** can be generated in the vacuum flash thermolysis of 5-(3-indolinylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione[60] and on opening the ring in the cyclobutenes **32** having a vinyl group in the 3-position[60–67] including the case where the group forms part of the composition of the benzene system[65,66] or a heterocyclic system.[65,67]

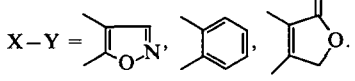


32 31

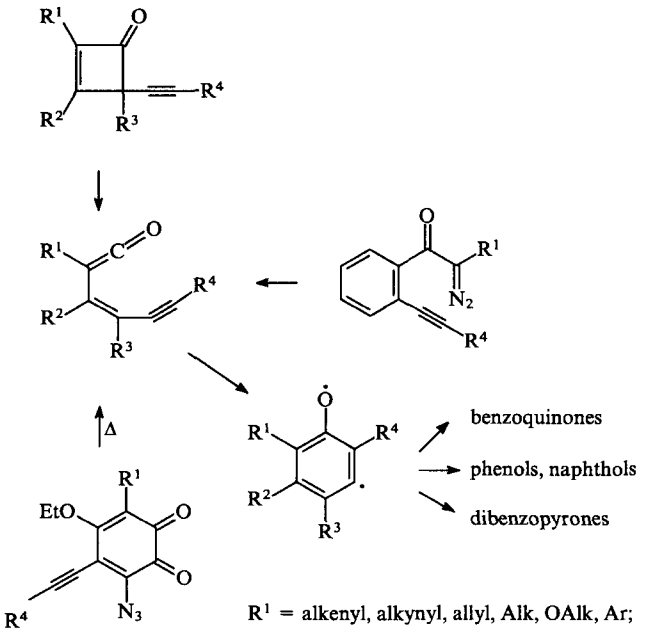
R^1 = Alk, Ar, alkynyl; X = H, Me_3Si;

R^2 = OAlk; Y = OMe, H;

R^3 = H, Cl, OAlk, OH, SPh;

X–Y = 

The replacement of the vinyl group by the ethynyl group does not prevent cyclisation.[61,65,68–73]



R^1 = Cl, R^4 = Ar.

R^1 = alkenyl, alkynyl, allyl, Alk, OAlk, Ar;

R^2 = Alk, OAlk, Ar;

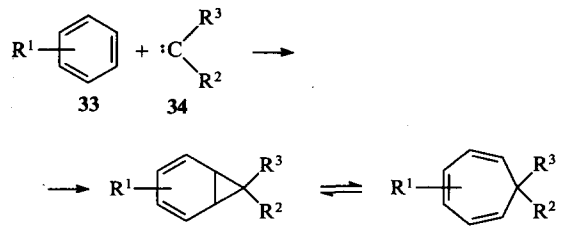
R^3 = OH, OAlk, CN;

R^4 = Alk, Ar.

The reactions of cyclobutenes described constitute general and flexible methods of synthesis of benzoquinones, phenols, naphthols, and related compounds, which are constituents of many biologically important substances. Thus the methods have been used in the synthesis of a nonsteroid antiinflammatory agent—(±)-naproxen.[74]

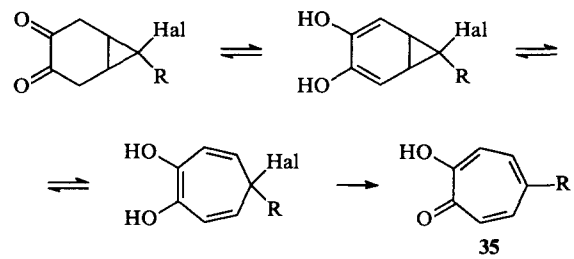
2. Reactions of cyclic compounds

In the general case, ER in cyclic systems are facilitated compared with acyclic systems. As a consequence of the high strain energy of the three-membered ring, the interconversions between cycloheptatrienes (CHT) and norcaradienes (NC) occupy a special place in this series. The opening of the norcaradiene ring is one of the stages in the syntheses of cycloheptatrienes from the benzene derivatives **33** and from the carbenes **34**[4,75,76] and of the hydroxytrienes **35**[77] and also in the rearrangements of the cycloheptatrienes **36** and **37**.[78,79]



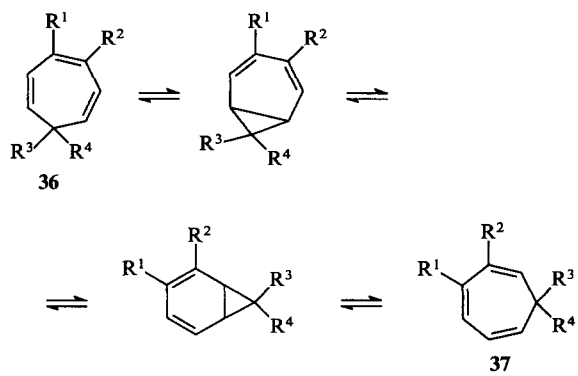
33 34

R^1, R^2, R^3 = H, Alk, Ar, CO_2Alk, CN.



35

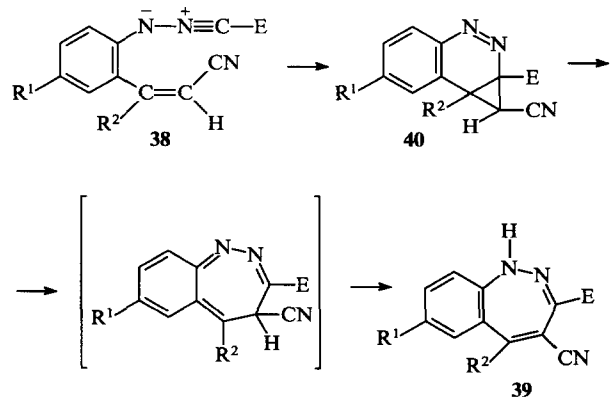
Hal = Cl, Br; R = Hal, H, Me_3Si.



36 37

R^1 = CO_2Me; R^2 = H, D; R^3 = Me, R^4 = CH_2OMe.

The rearrangement of the nitrile imines **38** to the benzodiazepines **39** also involves the 1,6-ER involving the opening of the norcaradiene ring.[80] The 2,3-diazanorcaradiene **40** formed in this reaction is stable; it is converted fully into the benzodiazepine **39** only on refluxing in benzene.[80]



38 40 39

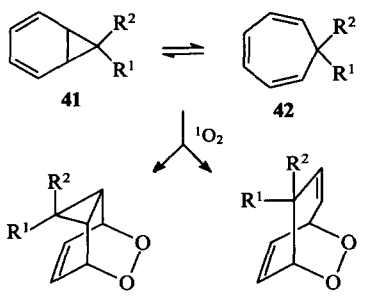
R^1 = H, R^2 = H;

R^1 = Cl, R^2 = Ph;

E = electron-accepting group.

The equilibrium between the norcaradienes and the cycloheptatrienes is as a rule appreciably displaced towards the latter and the concentration of the norcaradienes‡ in the mixture is low. Therefore, a very sensitive method is essential for the determination of the influence of the substituents on the equilibrium in the system.

The limitations in the use of NMR spectroscopy for these purposes have been noted by Adam et al.[82] At the same time, the method which they proposed for the determination of the position of equilibrium between the norcaradiene **41** and the cycloheptatriene **42** by using cycloaddition of singlet oxygen is inapplicable to the determination of equilibrium constants. It is in essence a variant of the method of competing reactions and makes it possible to determine the influence of substituents on the relative reactivities in the cycloaddition of the norcaradiene and the cycloheptatriene.[83,84]

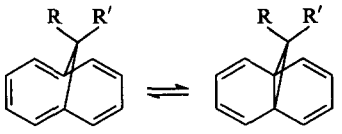


41 **42**

R^1, R^2 = H, Me, CO_2Me, Ph, 4-$MeO_2CC_6H_4$.

Kinetic studies have been made and quantum-chemical calculations of the activation parameters for this reaction have been performed.[85,86] According to kinetic data, the activation energy is only 7.7 kcal mol^{-1}.[83] Ab initio calculations in terms of the 4-31G basis set yield 7.3 and 2.3 kcal mol^{-1} for the forward and reverse reactions respectively in the cyclisation of the annulenes **43** to the norcaradienes **44**.[86]

The conversions of compounds **43** into compounds **44** are of great theoretical interest in connection with the aromatic properties manifested by the annulenes **43**, which contain 10 π-electrons.



43 **44**

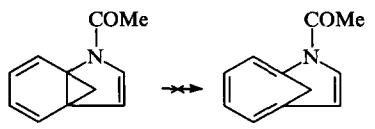
A topological approach has been applied to the study of the properties of 11-R, 11-R'-1,6-methano(10)annulenes.[21]

The existence of a critical bonding point in the 11,11-dicyano-derivative of compound **44** and in the β-phase of the crystals of the 11-cyano-11-methyl derivative of this annulene indicates a tricyclic structure for these substances. The authors[21] showed that the crystals are made up of two molecules; one has the norcaradiene structure **44** but with a low bond order, while the other has the annulene structure **43**. It is of interest to note that the bonds of the cyclopropane ring in compound **44** and the bridging bonds in compound **43** have an appreciable π-character and are conjugated with the π-system.[95]

The data concerning the influence of substituents on the equilibrium position between cycloheptatrienes and norcaradienes have been compiled by Marvell[4] and in subsequent publications.[87-92] The introduction of electron-accepting substituents in the 7-position, the inclusion of the π-bonds of the norcaradiene structure in the aromatic rings, and the introduction of bulky substituents in the 3- and 5-positions are all factors stabilising the structure of the norcaradiene. It has been shown that the insertion of yet another bridge between the 1- and 6-positions increases the stability of the norcaradiene form.[4,93-96] This feature is illustrated particularly clearly by the heteroatomic systems **45** and **46** incorporating sulfur and nitrogen atoms.[95,96] Thus the content of the tricyclic compound **45** in the equilibrium mixture is 84%, while that of compound **46** is 100%.



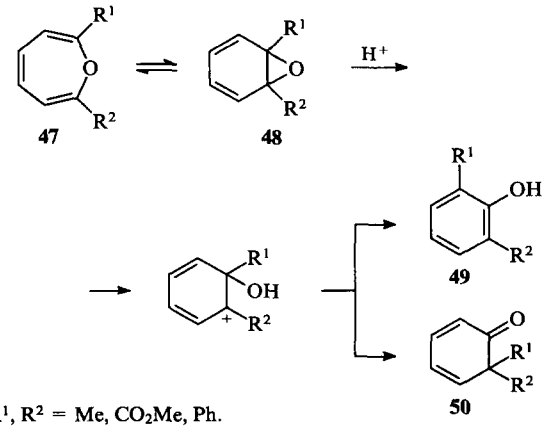
45



46

The interconversions of the heteroanalogues of the norcaradienes and cycloheptatrienes containing nitrogen,[97] oxygen,[98-100] sulfur,[101] phosphorus,[102] and boron[103] atoms instead of the methylene group have been described. The reactions of the oxygen-containing analogues have been most thoroughly investigated. It has been shown that arene oxides are the products of the metabolism of monocyclic and polycyclic aromatic compounds in plants, animals, and microorganisms[104,105] and that the reverse ring opening reaction to give oxepines is associated with their carcinogenic activity.[104,105]

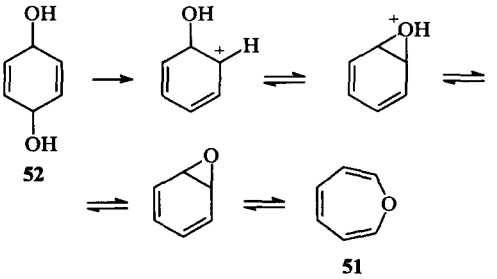
The conversion of the oxepines **47** into arene epoxides **48** is the first stage of the rearrangement of the oxepines **47** into the phenols **49** and the cyclohexadienones **50**[106,107] and also in the reactions of the aza-analogues of these compounds.[107]



47 **48** **49** **50**

R^1, R^2 = Me, CO_2Me, Ph.

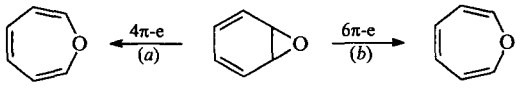
Conversely the retro-ER of the arene epoxides into oxepines is the last stage in the synthesis of type **51** compounds from compounds **52**.[108]



52 **51**

‡ The presence of the norcaradienes has been confirmed by NMR spectroscopy at low temperatures[81] and by X-ray diffraction of the xylene derivatives of this series.[93]

Benzene epoxide was first synthesised by Vogel et al.[109] about thirty years ago. It was shown that benzene epoxide is a little more stable than oxepine. The arene epoxide–oxepine equilibrium position is influenced by various factors: temperature, conjugation with the aromatic ring, the nature of the substituents, protonation, or complex formation. In the main, an analogy can be traced with the reactions of norcaradienes and cycloheptatrienes. The influence of various factors on the equilibrium between arene epoxides and oxepines has been examined in detail in a number of studies.[97,110–112] Two possible mechanisms of the conversion of aromatic arene epoxides into oxepines have been demonstrated[106] — the conrotatory opening of the oxirane ring (*a*) and the disrotatory opening of the cyclohexadiene ring (*b*).

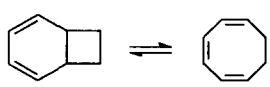


The choice in favour of the disrotatory 1,6-ER was made on the basis of the positive entropy of activation for the process determined from kinetic measurements and the lower activation energy than for the opening of the ring in oxiranes§ to give carbonyl ylides.[110–112] Kinetic studies on the 1,6-ER of arene epoxides and oxepines have been performed only for several compounds. This is associated mainly with the difficulty of determining the rates of fast reactions. The method for the determination of the rates of isomerisation of arene epoxides and oxepines involving the study of the degenerate racemisation of chiral arene epoxides at low temperatures, proposed by Jennings et al.,[112] is therefore a major achievement.

The relative stabilisation energies of arene epoxides and oxepines have been calculated with the aid of perturbation theory. The calculations explained the differences between the rates of racemisation of optically active polynuclear arene epoxides.[113]

Calculations for arene epoxides and oxepines by the AM-1 method and ab initio methods with various basis sets have been published quite recently. It has been shown that only the ab initio calculations in terms of the 6-31G basis set and involving the use of the third-order perturbation theory yield satisfactory heats of formation of benzene epoxide and oxepine.[23]

As a result of the lower strain energy of the cyclobutane ring compared with the cyclopropane ring, bicyclooctadienes are much more stable than bicycloheptadienes. The equilibrium between the bicyclooctadienes **52** and the octatrienes **53** and the rate of ER are influenced by various factors: electronic[4–35] and steric properties of the substituents,[114] the strain energy of dienes and trienes with cisoid double bonds, conjugation of double bonds with aromatic π-systems,[32] etc.



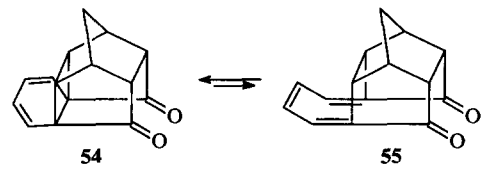
52 **53**

Apart from their theoretical interest, the 1,6-ER of cyclic trienes have also a considerable practical importance. Thus they have been used in the synthesis of vitamin A[115] and of endiandric acids.[116,117]

An increase in the size of the ring condensed with the cyclohexadiene leads to a greater stability of the bicyclic form compared with the monocyclic form,[4] which promotes the cyclisation of isomeric trienes. Thus compound **5a** cyclises at 75 °C,[26] while compound **5b** cyclises at room temperature.[27,28] The transoid trienes **10** cyclise even more readily (at −55 °C).

§ The isomerisation of the optically active *trans*-2-phenyl-3-(*p*-tolyl)-oxirane (conrotatory opening of the oxirane ring) takes place at high temperatures (180–247 °C) and has E_a = 35.9–41.1 kcal mol^{-1} and ΔS = −2 to +2 kcal mol^{-1} K^{-1}.

In conclusion of this section, we may note that in a later study[118] the authors were able to observe the 1,6-ER in the propellane systems **54** and **55**.



54 **55**

VI. Photochemical processes

It has been shown by means of a large number of examples that the interconversions between cyclohexa-1,3-dienes and hexa-1,3,5-trienes are effected photochemically as conrotatory processes.[4] However, it is claimed[16] that the cyclisation process does not involve the retention of the C_2 symmetry axis. The transition state on the potential energy surface (PES) in the ground state and the state corresponding to the minimum on the PES for the excited state are asymmetric.

It has been shown that these processes proceed via a ππ* excited state and are photochemical singlet reactions.[1–3,14,40,41] Kinetic[40,41] and quantum-chemical studies[14,41] permitted the conclusion that the photochemical opening of the ring in cyclohexadienes does not take place adiabatically and constitutes a more complex process. The first stage involves photoexcitation and transition from the ground state ($1A_1$) to the excited state ($1B_2$), in the second stage there is a transition (with a small energy barrier) to the next excited state ($2A_1$), then there is a nonadiabatic transition onto the potential surface for the conrotatory reaction, and the final stage involves the formation of the triene in the ground state (Fig. 1).

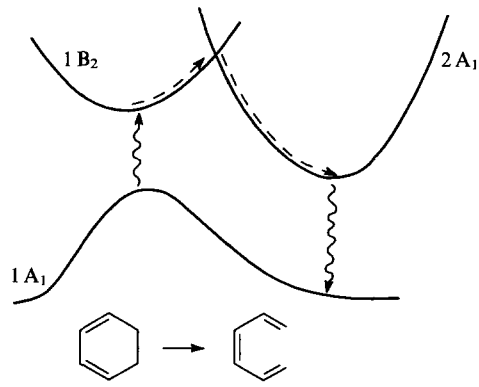
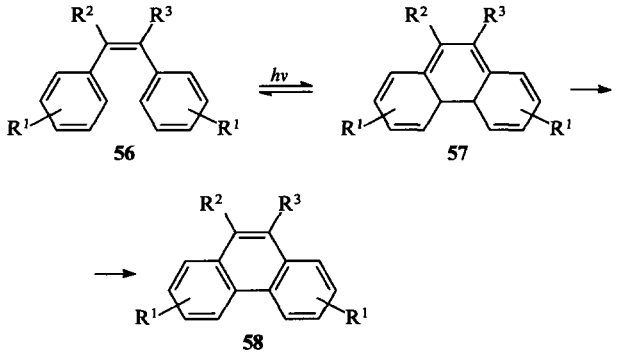


Figure 1. The mechanism of the photochemical opening of the ring in cyclohexadienes. The potential surfaces for the $1A_1$, $2A_1$, and $1B_2$ states are shown.

The photochemical reactions of simple cyclohexadienes and hexatrienes described by Havinga and coworkers[119–121] and also by their successors[122–124] have been the subject of a series of reviews[4,124–126] and we shall therefore not consider them in detail.

In describing thermal 1,6-ER, it was noted that the processes proceeding with breakdown of the aromaticity of the rings incorporating the double bonds of the triene or hexadiene system are hindered. In contrast to the thermal reactions, the opening of the cyclohexadiene rings and the cyclisation of hexatrienes are readily effected photochemically also in the case when one of the double bonds enters into the composition of an aromatic cyclic system.[17]

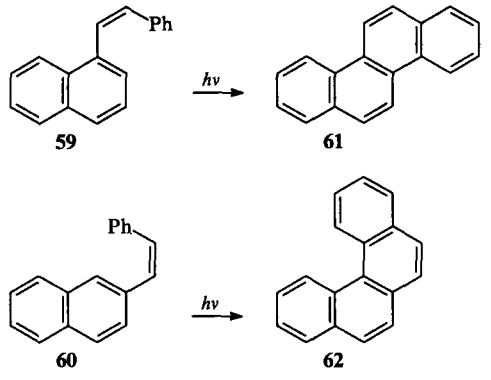
The photocyclisation of the substituted *cis*-stilbenes **56** to 4*a*, 4*b*-dihydrophenanthrenes **57**, which are unstable and are converted into the polynuclear arenes **58** in the presence of atmospheric oxygen or iodine, has been thoroughly investigated and is widely used in organic synthesis.[4]



56 **57** **58**

R^1, R^2, R^3 = H, Alk, Ar, OAlk, and others.

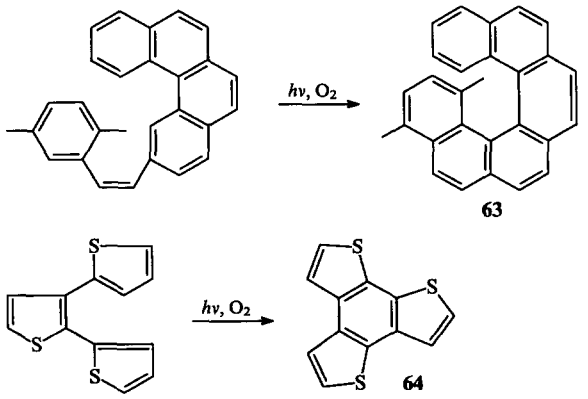
This reaction has been extended also to other arylhexatrienes. Thus the cyclisation of α- or β-(phenylvinyl)naphthalenes **59** and **60** leads to the formation of chrysene **61** and benzo[*c*]phenanthrene **62**.



59 **61** **60** **62**

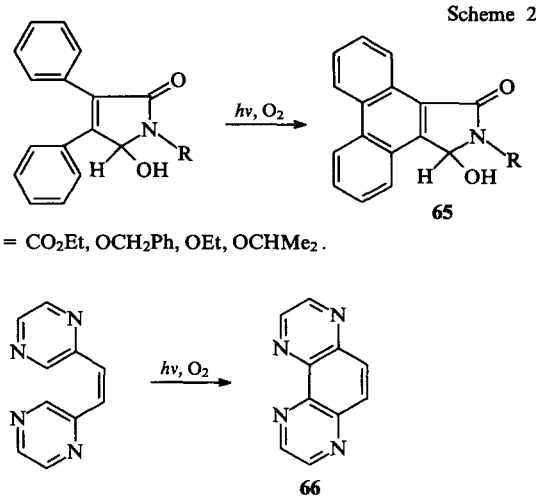
Photocyclisation is used to obtain the helicenes **63** (including the optically active compound),[127] the heterocyclic compound benzotrithiophene **64**,[128] the phenanthropyrrolines **65**, and 1,4,5,8-tetraazaphenanthrene **66** (Scheme 2).[129,130]

Scheme 2



63 **64**

Scheme 2 (cont.)

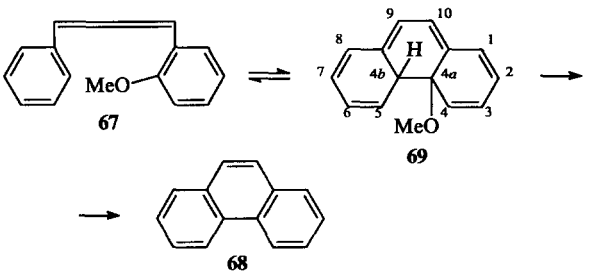


65

R = CO_2Et, OCH_2Ph, OEt, $OCHMe_2$.

66

Mallory et al.[131] note that *meta*-substituted stilbenes give rise to mixtures of isomers which are difficult to separate into their components. They showed that the introduction of the methoxy-group leads to the regioselective cyclisation of compound **67** with participation of the substituted atom; the subsequent elimination of methanol, which is facilitated by the addition of a solution of sulfuric acid in *tert*-butyl alcohol, gives the individual phenanthrene **68**.



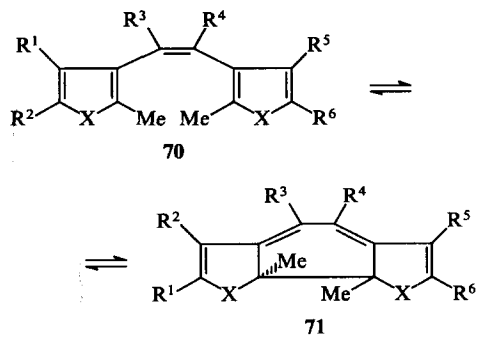
67 **69** **68**

When amines are used in the absence of oxygen, aromatic dihydro-compounds of type **69** are obtained.[132] It has been shown that the amine behaves as a base and interacts with the 4*a*, 4*b*-dihydrophenanthrene formed initially, promoting proton transfer from the C(4*a*) atom to the C(4) atom. Propanethiolate promotes proton transfer to the 9-position, whilst sodium methoxide promotes such transfer to the 2-, 4-, and 9-positions, which leads ultimately to the formation of 1,4- and 9,10-dihydrophenanthrenes.[133]

In connection with the discovery of the photochromic properties of 1,2-diheteroarylethenes, a number of studies on the synthesis of a wide variety of compounds of this series have been carried out.[16,134–137] It has been shown that 1,2-diheteroarylethenes **70** undergo a photoinduced thermally irreversible cyclisation to the coloured compound **71**. It is interesting to note that the acquisition of a colour–decolorisation cycle may be repeated more than 10 000 times without appreciable loss of efficiency.[116]

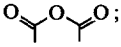
In contrast to other representatives of this series, compounds **71** [X = NMe; R^1, R^2 = $-(CH{=}CH)_2-$; R^3 = R^4 =CN; R^5 = R^6 = Me] have no thermal stability, like dihydrophenanthrenes,[4] while compounds of type **72**, containing imidazo[1,2-*a*]-pyridine residues, do not cyclise, undergoing the photoinduced *Z*–*E* isomerisation to compounds **73**[135] and are therefore of no interest as photochromic materials of this type.

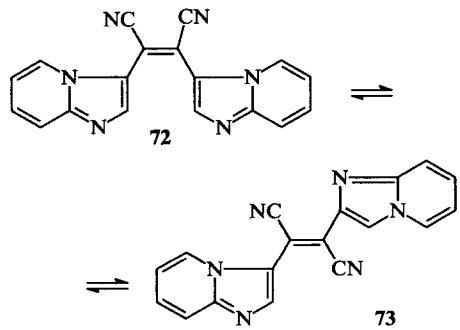
The replacement of one imidazopyridine fragment in compound **72** by a thiophene fragment facilitates the 1,6-electrocyclic reaction.[135]



70 ⇌ 71

$R^1+R^2 = R^5+R^6 =$ 

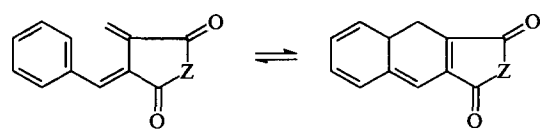
R^3, R^4 = CN, ; X = S, Se.



72 ⇌ 73

Nakamura and Irie[17] analysed the results of semiempirical calculations in terms of the MNDO approximation carried out for 1,2-di(3-furyl)-, 1,2-di(3-thienyl)-, 1,2-di(3-pyrrolyl)-, and 1,2-diphenyl-ethenes and showed that the energy barrier in the ring opening reaction is correlated with the difference between the energies of the ground states of the cyclic and open-chain forms; the smaller this difference, the higher the barrier.[17] The difference between the energies of the cyclic and open-chain forms is in its turn correlated with the aromatic stabilisation energy of the cyclic substituents. Thus the higher thermal stability of 1,2-diheteroarylethenes compared with 1,2-diarylethenes can be explained by the lower aromaticity of the heterocyclic compounds compared with benzene.[17]

The phenomenon of photochromism in the fulgides **74** and fulgimides **75** is also due to the 1,6-ER of hexatrienes.

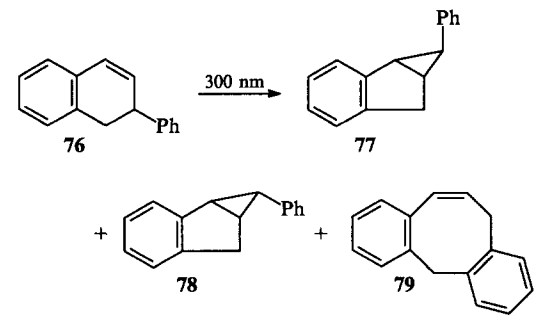


74, Z = O. **75**, Z = NR (R = Ph, Bz, Alk).

Reactions of this type have been described in a review[138] and those of the hetero-analogues of fulgides and fulgimides have been described in a number of other communications[139-144] and are therefore not considered here.

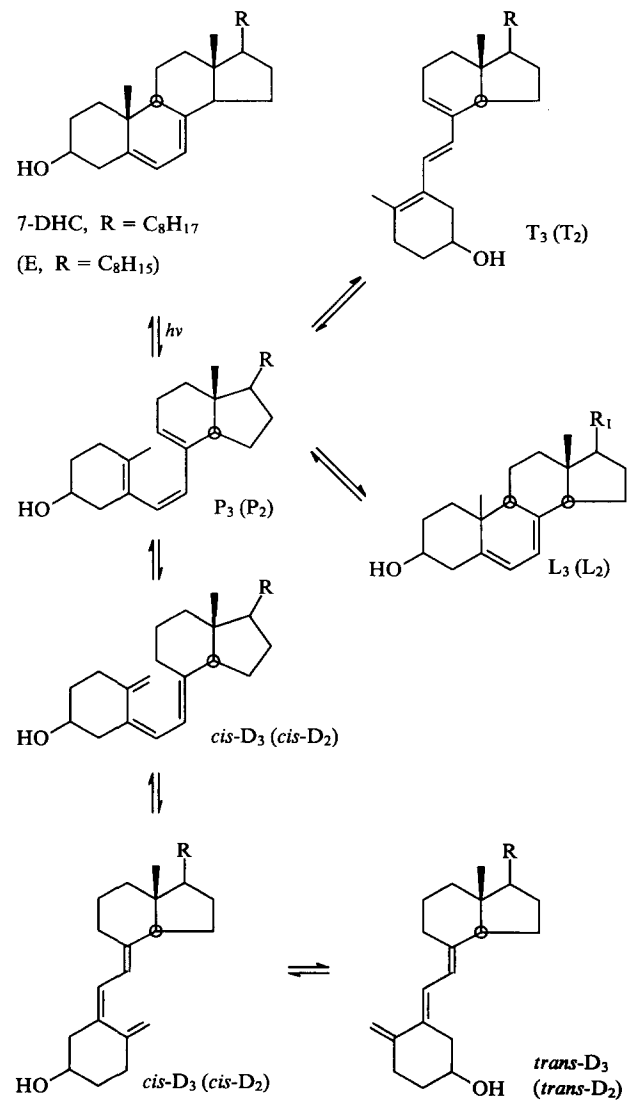
The ring opening reaction of cyclohexadienes, which occurs on UV irradiation, is used to synthesise trienes in the *cis*-(*Z*)-*cis*-conformation.[4] The ring-opening process is usually accompanied by side reactions — *Z*–*E* isomerisation, sigmatropic shifts of hydrogen atoms, and also 1,4- and 1,6-cyclisation.[122]

Thus irradiation of 2-phenyl-1,2-dihydronaphthalene **76** with UV light at a wavelength of 300 nm leads to three primary photoproducts: *endo*- and *exo*-6-phenylbenzobicyclo[3.1.0]hex-2-enes **77** and **78** and 7,12-dihydrodibenzo[*a*,*b*]cyclooctatetraene **79**.[44]



It has been shown[44] by means of experiments with 3,4-d_2-labelled specimens of compound **76** that the two isomers (compounds **77** and **78**) are formed via two paths — via the mechanism of the di-π-methane rearrangement and as a result of the electrocyclic ring opening with subsequent photocyclisation.

The complex photochemistry of 7-dihydrocholesterol (7-DHC) and ergosterol (E) became understood as a consequence of the studies of Havinga and coworkers.[119,120] Together with the electrocyclic ring opening and the formation of the (*Z*)-trienes P_2 and P_3, *Z*–*E* isomerisation, 1,4-ER, dimerisation, and sigmatropic transformations take place. The ratios of the products formed depend on the temperature, the diene concentration, and the wavelength of the irradiating light. The following scheme gives an idea about the photochemistry of the process (at a temperature below 0 °C):



It was shown that the singlet and triplet transformations of 7-DHC lead to different products.[119] Photolysis in the range 271–310 nm gives relatively high yields of P_3 (provitamin D); irradiation at shorter wavelengths leads to the predominance of tachysterone (T_3), while irradiation at longer wavelengths gives rise to compound L_3.[145,147]

In the synthesis of vitamin D, the photochemical reaction is usually arrested at 50% conversion of 7-DHC and provitamin D (P_3) is isolated by fractional crystallisation. The provitamin is then converted into the target product as a result of a 1,7-sigmatropic shift.

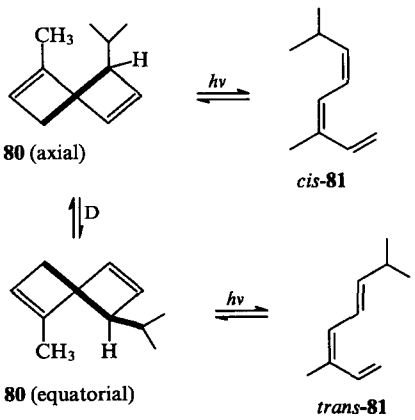
It has been noted[145,148] that, when the technique involving laser photolysis with subsequent irradiation by light at wavelengths of 248 and 473 nm, 248 and 353 nm, and 254 (300) and more than 330 nm is used, predominantly P_3 (P_2) is formed.

The photochemistry of vitamin D stimulated studies on the photochemical reactions of simple hexa-1,3,5-trienes and related systems. The principle of Non-Equilibriation of Excited-state Rotamers (NEER) was developed as a result of these investigations.[119,149,150] According to this principle, the lifetime of the singlet state is not long enough for the isomerisation of different conformers, so that conformers of each type give rise to their own assortment of products.

Thus the ratios and compositions of the substances formed on photolysis of hexatrienes are determined by the isomeric compositions of the conformers of the initial compound in the ground state.[119]

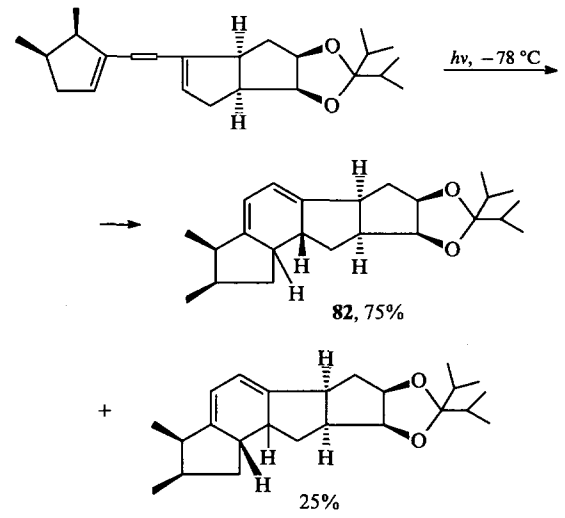
Later the NEER principle was extended to simple hexatrienes. It was shown that an increase in the bulk of the substituents in the 2- and 5-positions in the triene system increases the fraction of the *cis*-(*Z*)-*cis*-isomer and therefore promotes cyclisation.[151]

In their study of the influence of the conformational control on the ratio of the products formed on photolysis of α-phellandrene **80**, Baldwin and Krueger[152] demonstrated the applicability of the NEER principle to retro-ER.[152] They showed that the fraction of the isomer with the axial isopropyl group increases with decrease in reaction temperature and there is a consequent increase in the fraction of the *cis*-isomer of compound **81**.

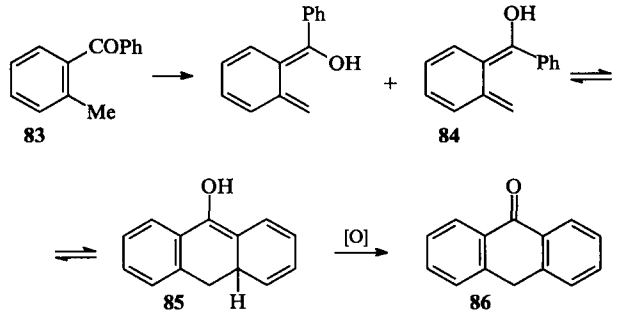


It is essential to note that, in conformity with the orbital symmetry conservation rules, the formation of both *cis*- and *trans*-**81** from the axial isomer of compound **80** is allowed. The preferential formation of *cis*-**81** from the axial isomer of compound **80** and of *trans*-**81** from the equatorial isomer served as a basis for the principle, formulated by Baldwin,[152] which states that the mode of the reaction corresponds to the conformation of the diene in the ground state. When a triene is formed via the 'corresponding' path (the formation of *cis*-**81** from the axial **80**), the *p*-orbitals generated began to overlap with the existing π-system in the early stages of the reaction, whereas in the operation of the 'noncorresponding' path (the formation of *trans*-**81** from the axial **80**), they should pass through the node in the plane of the π-system. The concepts introduced by Baldwin are very closely related to the term 'torquoselectivity' introduced by Houk in a study of the thermal opening of the ring in cyclobutenes.[7–9]

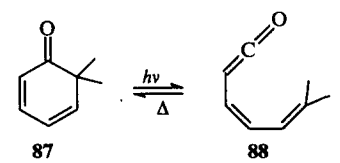
By using the correspondence principle, Whitesell et al.[150] achieved the stereoselective synthesis of the principal fragment in ikarugamycin **82**.



Hexatrienes containing a hydroxy-group in the 5-position are unstable owing to their conversion into the keto-form. However, by irradiating 2-methylbenzophenone **83**, Wilson et al.[153] were able to generate compound **84**, which cyclises, following the absorption of a second photon, to compound **85**, which is oxidised to anthrone **86**.[153]



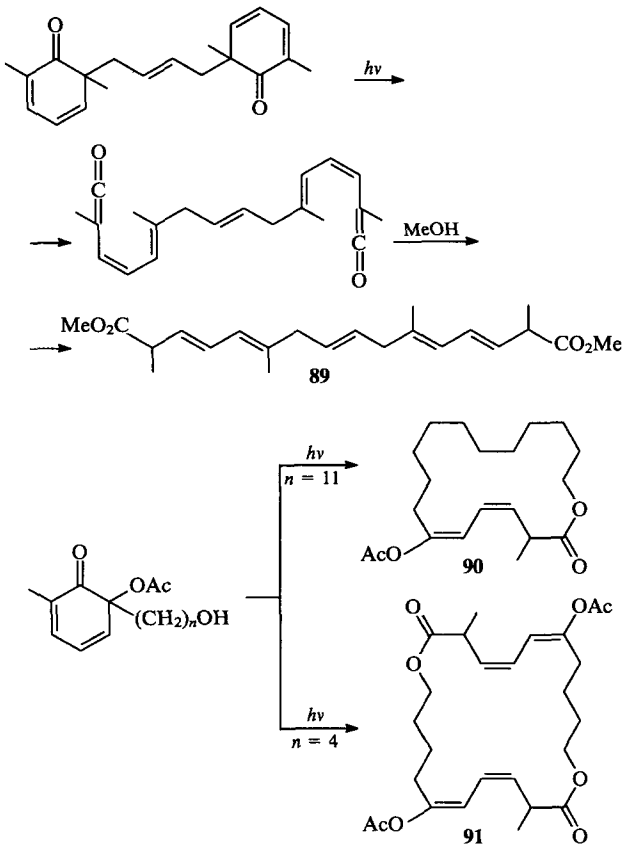
The photochemical opening of the ring in cyclohexa-2,4-dienone **87** results in the formation of the triene **88** containing the ketene group.[154,155]



The reaction proceeds via a n,π^* excited singlet state. The ketene **88** is thermally unstable and is reconverted into the initial compound,[156] but it may be 'trapped' by different nucleophiles.

Since the initial cyclohexadienones **87** are readily available, this reaction constitutes a valuable synthetic method for the preparation of diverse organic compounds with unusual structures.[157]

The most striking examples illustrating the effectiveness of this method are the syntheses of dimethylcrocetin **89**, the pigment saffron,[158] and the macrocyclic lactones **90** and **91**.[159]



VII. 1,6-Electrocyclic reactions in heteroatomic systems

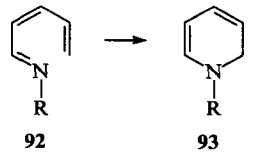
The introduction of heteroatoms into a conjugated π-system hardly alters the symmetry and mechanism of the cyclisation. The substitution of the terminal methylene group by a heteroatom diminishes the exothermicity of the reaction and lowers the barrier to the cyclisation process.[4,16] It has been noted that the introduction of heteroatoms into the terminal positions in the triene system diminishes the difference between the activation energies for the processes proceeding via allowed and forbidden paths.[16] When two heteroatoms are introduced into the terminal positions, the cyclic form is strongly destabilised and the open-chain structure becomes more stable.[4,16] Analysis of the correlation diagrams for the electronic states of the cyclic and open-chain forms leads to the conclusion that the cyclisation of 1,6-dioxatrienes is prohibited in the ground state in both ways — disrotatory and conrotatory.[160] The data on the 1,6-ER of heteroatomic systems are divided arbitrarily into subsections depending on the type (nitrogen, oxygen, sulfur) and number of heteroatoms.

1. Reactions of nitrogen-containing compounds

A nitrogen atom may be introduced into any position in hexa-1,3,5-triene without a significant alteration of the π-system. ER have been described in the literature for all the isomeric mono-azatrienes.[4]

In the general case, the 1-azahexatrienes **92** are less stable than their cyclic isomers — 2-dihydropyridines **93** (Scheme 3).[4]

Scheme 3

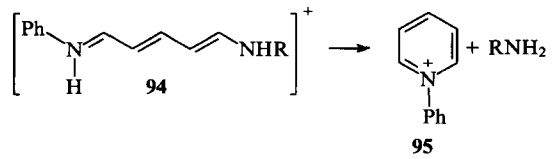


R = H, Alk, Ar.

Reactions involving the opening of the rings in pyridinium salts by nucleophiles,[4] the cyclisation of Konig's salts,[161] rearrangements of the Dimroth[162] and Kost–Sagitullin[163] types, the transformation of oxazines into pyridines,[164] and nucleophilic substitution in heteroaromatic compounds via the ANRORC mechanism[165] have been thoroughly investigated. All these reactions include at least one 1,6-ER of 1-azahexatrienes.

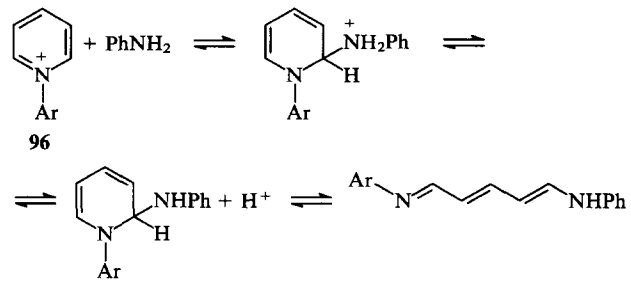
It has been shown that the cyclisation of Konig's salts **94** to the pyridinium salts **95** is catalysed by both bases and acids.[4]

The *cis–trans* isomerisation of compound **94** takes place very readily; E_a is only 6 kcal mol^{-1}.[4] Unfortunately all the atoms in compounds **94** and **95** are located in one plane and their structure does not therefore yield information about the stereochemistry of the process.



Numerous studies, surveyed in Marvell's book,[4] have been devoted to the reactions involving the opening of pyridinium rings by nucleophiles.

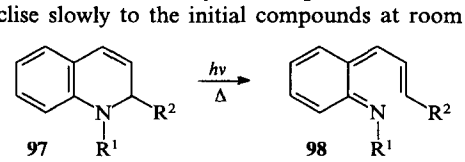
Kinetic investigations indicate the acceleration of the reaction after the introduction of electron-accepting substituents into the *para*-position in the phenyl group. Thus the opening of the ring in dinitrophenylpyridinium **96** by sodium hydroxide is 10^6 times faster than in the unsubstituted phenylpyridinium.[4] It has been noted[166] that the reaction mechanism may change when the pH of the medium is altered. The ring opening reaction is apparently fast and is not the rate-limiting stage in the overall process.



Ar = 2,4-$(NO_2)_2C_6H_3$.

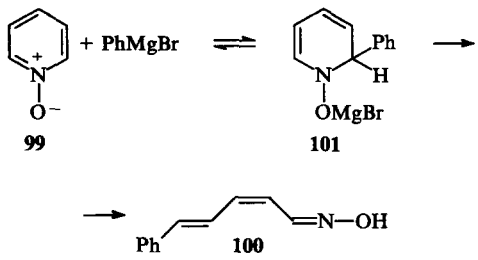
It has been observed that the Schiff bases of retinal analogues cyclise extremely readily to dihydropyridine analogues.[167] It has been shown[167] that the rate of the process is influenced by steric and conformational factors. Data concerning the use of retinal azomethines as models simulating the spectroscopic and chemical properties of certain pigments of halobacteria, particularly bacteriorhodopsin, were analysed in the same communication.[167]

When the dihydroquinolines **97** are irradiated with UV light at 196 °C, the monocyclic compounds **98** are formed. These cyclise slowly to the initial compounds at room temperature.[4]



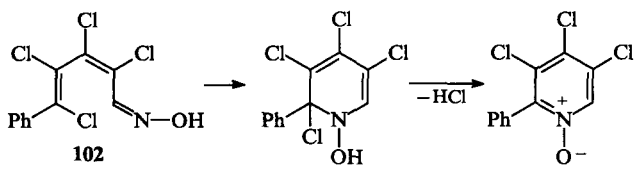
R^1 = COOEt, CN; R^2 = CN, OH.

On interaction with a Grignard reagent, pyridine *N*-oxide **99** affords the dienyloxime **100**.[4] The last stage of this process is the electrocyclic opening of the ring in the intermediate dihydropyridine **101**.

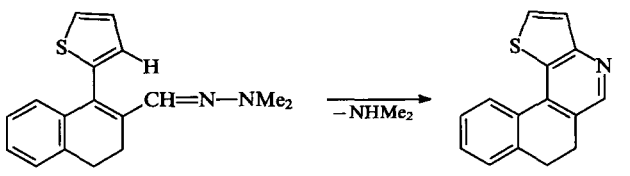


99 101 100

Like the hydrazones **103** having double bonds in the *cis*-positions, the dienyloximes **102** are capable of being converted into dihydropyridines. The latter may be stabilised by the abstraction of a water or hydrogen chloride molecule[4] and, in the case of the hydrazone **103**, by the abstraction of dimethylamine.[168,169]



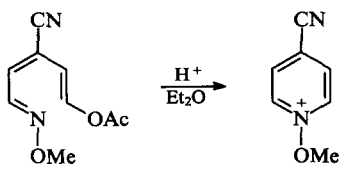
102



103

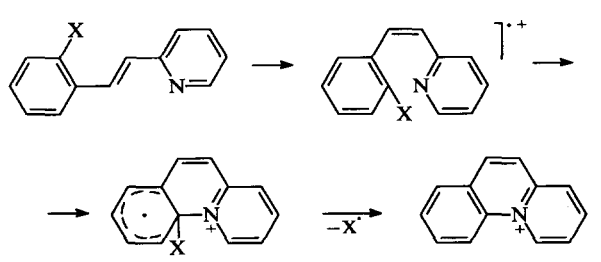
The cyclisation reactions of the trienes **102** and **103** apparently take place with a low activation energy E_a and the rate of the overall process is limited by other stages.

The formation of the pyridinium salts **104**, additionally stabilised as a consequence of their aromatic properties, is the driving force in the cyclisation of compounds **105** in acid media.[170]



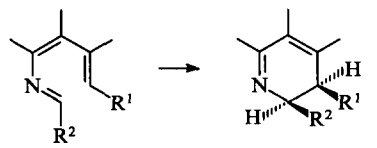
105 **104**

A single study[171] of 1,6-ER with participation of radical species containing the 1-azahexatriene system has been published.



X = H, Me, F, Cl.

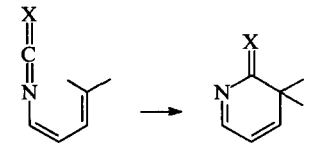
The introduction of a nitrogen atom in the 2- and 3-positions in the hexatriene system 'perturbs' the orbitals only slightly and should not alter the cyclisation mechanism. The results of calculations and experiments[4] confirm this conclusion and indicate a disrotatory mechanism for the cyclisation of 2-aza-hexa-1,3,5-trienes **106**.



106

R^1, R^2 = Alk.

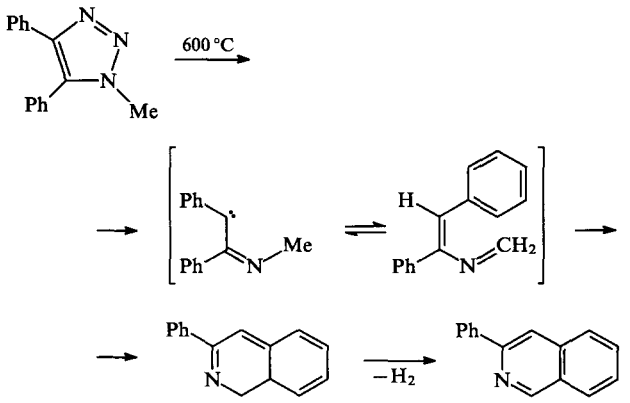
The cyclisation of the dienyl isocyanate **107**[172] and of the carbodiimide **108**[173,174] can take place without rotation relative to the N=C bond by analogy with the 1,4-ER of iminoketenes.[5]



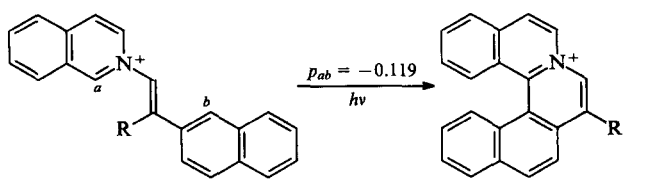
107, X = O.

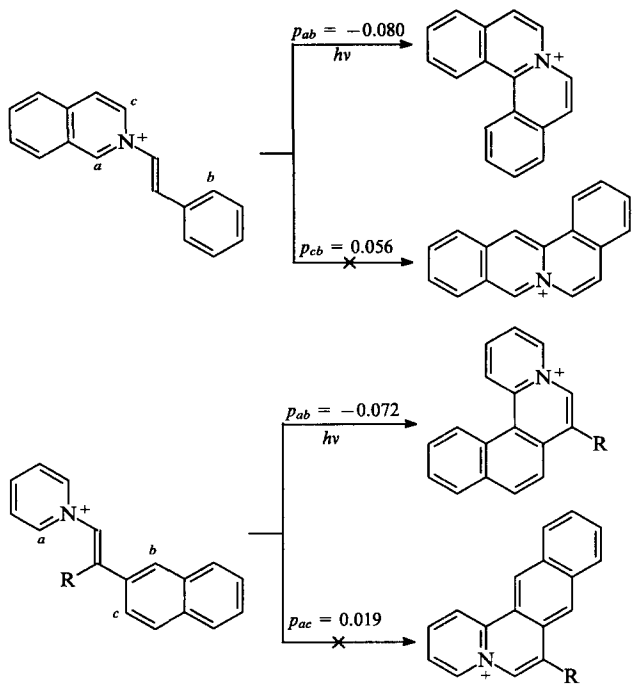
108, X = NPh.

The thermal transformation of 1-methyl-4,5-diphenyl-1,2,3-triazoles into 3-phenylisoquinolines can apparently also include the 1,6-electrocyclic closure of the 2-azatrienyl system.[175,176]

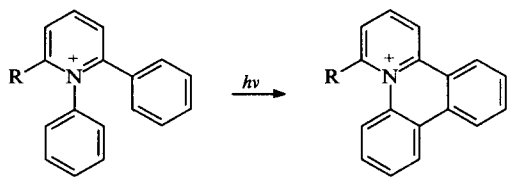


There are examples of the cyclisation of 2-azatrienes containing a quaternary nitrogen atom in the molecule.[4,177,178] It has been shown[177,178] that the order of the bond (p) between the atoms being linked (C_a, C_b, and C_c) must be negative for cyclisation to occur.





The photocyclisation of compounds **109**, containing the azoniahexa-1,3,5-triene system, has been studied in detail by Dorofeenko and coworkers[179] and their successors[180] and constitutes yet another example of 1,6-ER.

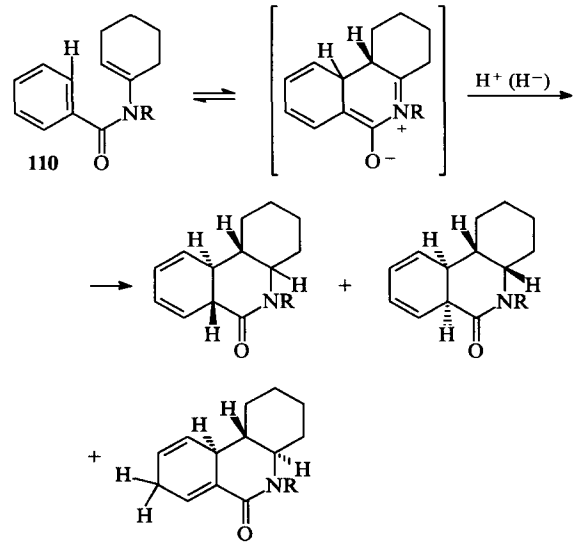


109

R = Me, COOH, Ph.

There exists a single study[181] on the basis of which one may reach a conclusion concerning the mechanism of the cyclisation of 3-azahexatrienes. The authors[181] showed that reductive photocyclisation of the enamides **110** takes place in a conrotatory manner in conformity with the orbital symmetry conservation rules (Scheme 4).[1-3]

Scheme 4



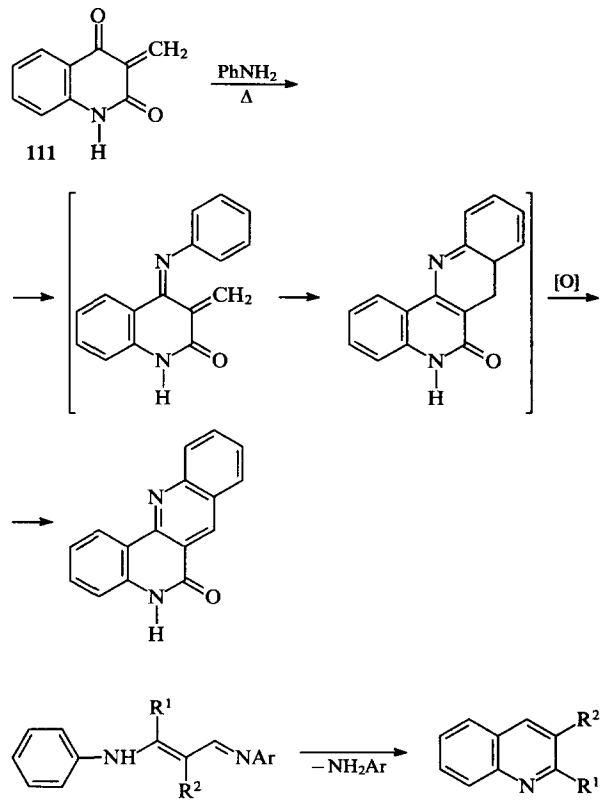
110

R = Alk, Ar.

The photocyclisation of enamides[182] has been used by the same workers to synthesise the alkaloid naucleficine.

The dihydropyridines **111**, formed on thermal cyclisation of 3-azahexatrienes, are converted into aromatic compounds as a result of the oxidation or elimination of low-molecular-mass products, which hinders the study of the stereochemistry of this reaction (Scheme 5).[4,183]

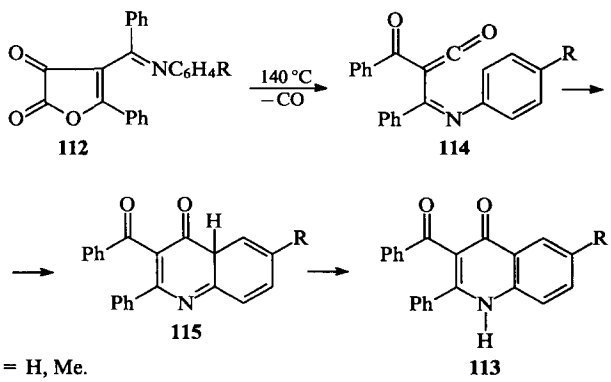
Scheme 5



111

R¹, R² = H, Me.

The transformation of the furandione **112** into the quinolinone **113** apparently involves the cyclisation of the iminoketenes **114** to the hydropyridine **115**. The latter is stabilised as a result of the 1,3-sigmatropic shift of a hydrogen atom.[184]



112 **114**

115

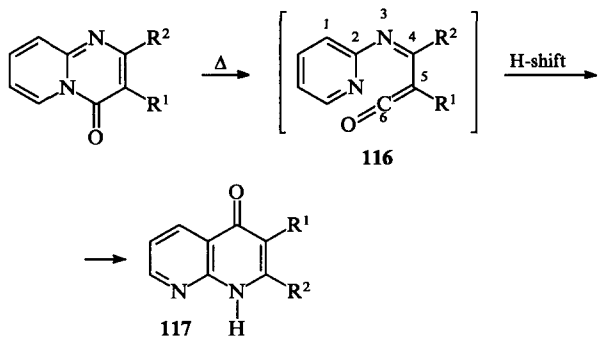
R = H, Me.

113

The formation and 1,6-ER of the iminoketenes **116** constitute the basis of the rearrangement of pyrido[1,2-*b*]pyrimidines to pyridopyridones **117**.[185]

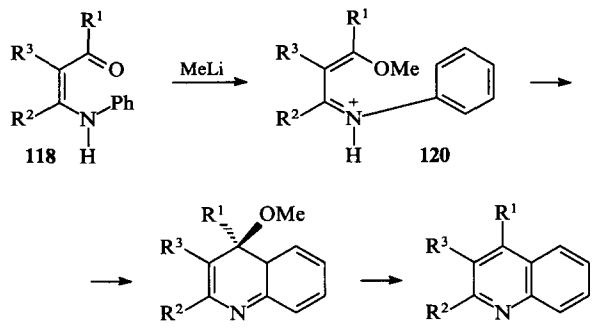
It has been shown[186] that the methylation of the ketoenamines **118** by dimethyl sulfate leads to the quinolines **119**.

It has been suggested[186] that the reaction proceeds via the intermediate cation **120**. Taking this into account, one may conclude that the cyclisation of 3-azoniahexatrienes may be achieved not only photochemically but also thermally.



116

117

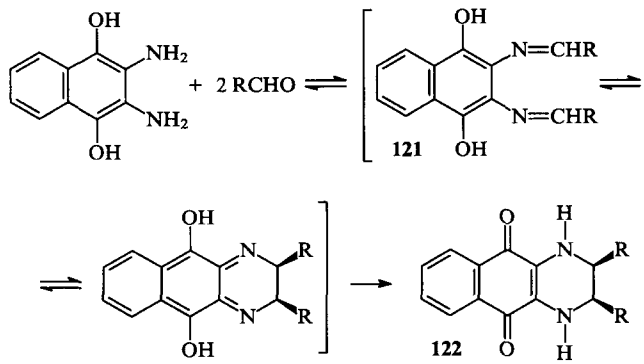


118 120 119

R^1, R^2, R^3 = H, Me, Bu^t.

It has been demonstrated with the aid of quantum-chemical calculations that the substitution of two CH groups in the 2- and 4-positions and also in the 2- and 5-positions in the hexatriene system should not alter the mechanism of the cyclisation reaction.[171] Experimental data fully support these conclusions (Scheme 6).[4]

Scheme 6



121 122

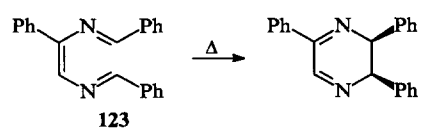
R = 2-HOC$_6$H$_4$, 2-OH-3-MeOC$_6$H$_3$,

2-OH-4-MeOC$_6$H$_3$, 2-OH-5-MeOC$_6$H$_3$,

4-MeC$_6$H$_4$, 4-NH$_2$C$_6$H$_4$.

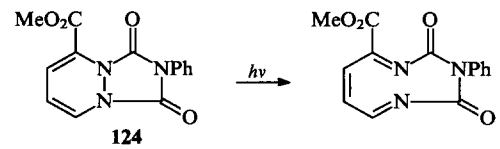
It has been shown[187] that the azomethine imines **121** cyclise via a disrotatory process with the ultimate formation of the quinones **122**. Freeman and Kim demonstrated the possibility of the occurrence of this reaction for the acyclic 2,5-diaza-1,3,5-trienes.[188]

A more rigorous demonstration of the disrotatory cyclisation mechanism has been achieved by Padwa et al.[189] in a study of the cyclisation of the triene **123**.



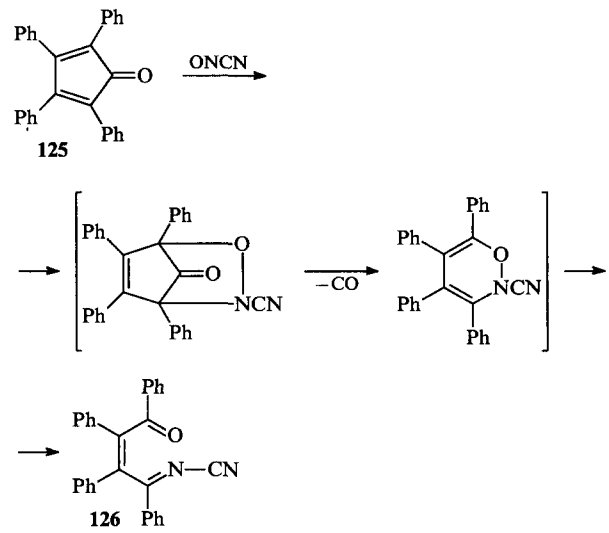
123

The photochemical opening of the ring in the dihydropyridazine **124** is an example of a reaction involving the 1,6-diazahexatriene system.[190]



124

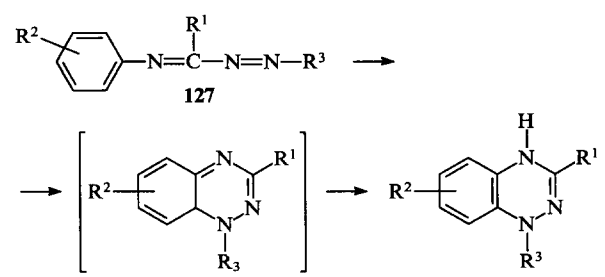
1,6-Diazahexa-1,3,5-trienes are more stable than their cyclic isomers. This apparently applies also to systems having other heteroatoms with lone pairs in the terminal positions. Thus the reaction of the cyclopentadienone **125** with nitrosocyanogen leads to the formation of 1-oxa-6-azahexa-1,3,5-triene **126** in a pure form and in a high yield.[191]



125 126

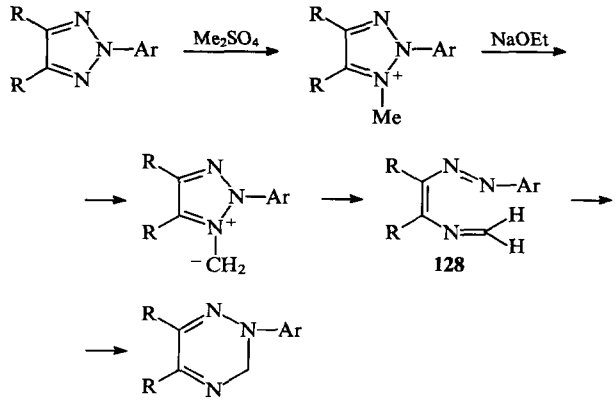
Nucleophilic substitution in pyramidines, which proceeds via the ANRORC mechanism and has been discovered and studied in detail by van der Plas and coworkers,[165,192] includes the 1,6-ER of 1,5-diazahexatrienes as one of the stages.

The cyclisations of 1,4-diaryl-1,2,4-triaza-1,3-dienes **127**,[193] 1-aryl-1,2,5-triazadienes **128**,[175,176] as well as aromatic and heteroaromatic diazonium salts belong to the class of 1,6-ER of triene systems with three nitrogen atoms. They will be examined in the next section.

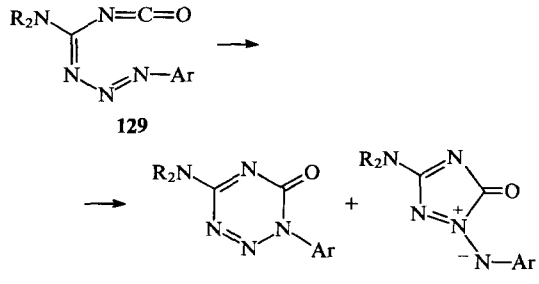


127

R^1, R^2, R^3 = H, Me, Ar, COMe, COPh, CO_2Alk.



The cyclisation of the isocyanates **129** is an example of the ER of trienes with four nitrogen atoms.[194]



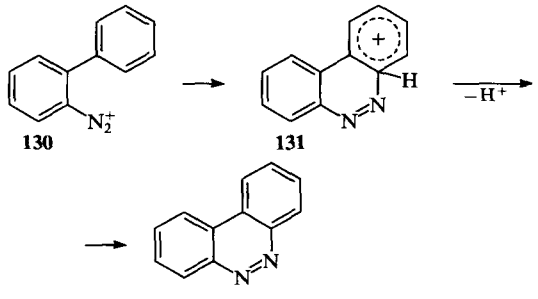
2. Cyclisation of heterocyclic diazo-compounds and diazonium salts

One of the possible mechanisms of the cyclisation of aromatic diazonium salts and heterocyclic diazo-compounds, in the *ortho*-positions of which there are groups containing multiple bonds, involves a monorotatory 1,6-electrocyclic reaction. This reaction is used widely in the synthesis of a wide variety of six-membered heterocyclic compounds such as pyrazines, v-triazines, and thiadiazines.

Since these processes have many features in common, they are described in a separate subsection.

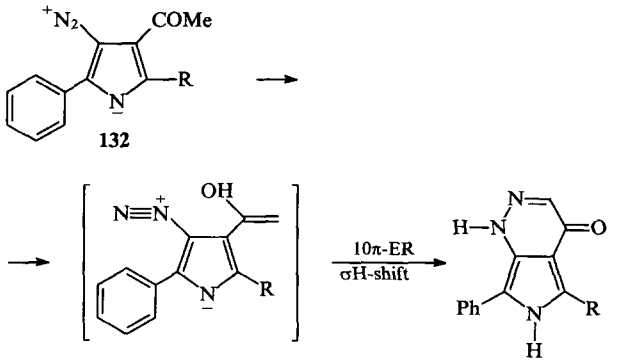
a. The formation of the N–C bond

The cyclisation of diazonium salts and heterocyclic diazo-compounds containing a vinyl group in the β-position (the Widman–Stoermer reaction) is treated as an intramolecular azo-coupling for the aryl derivatives **130**.[195–198]



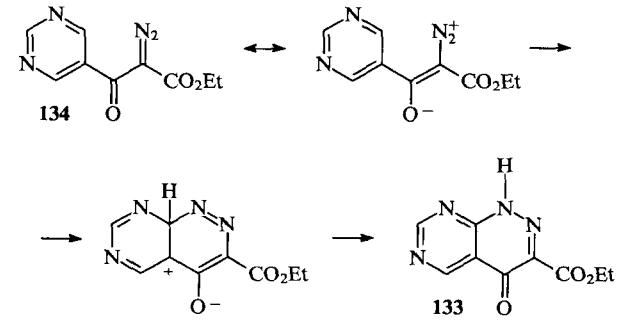
Unfortunately, experimental and theoretical studies on the mechanisms of this reaction are not described in the literature; the intermediate complexes **131** have not been characterised, the influence of the π-system on the energy relations of the cyclisation reaction has not been elucidated, and kinetic studies have not been carried out.

Presumably, the diazoketones **132** cyclise via a similar mechanism. It is of interest to note that the methylketo-group, tentatively in the enolic form, and not the aromatic ring, participates in the reaction.[199]



R = H, Me.

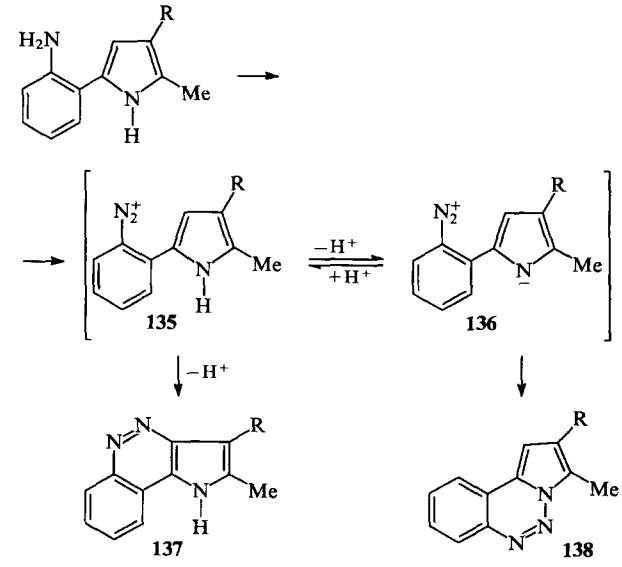
The occurrence of this reaction requires the presence of sulfuric acid. Thus, on heating in DMF, the initial compound **132** remains unaltered.[199]



The condensed pyridazines **133** are also formed on cyclisation of pyrimidinyl diazoketones **134**.[200,201]

If the molecule of the diazo-compound contains a pyrrole ring in the *ortho*-position relative to the diazonium group, the reaction can proceed via two paths, depending on the pH of the medium, with formation of a C–N or N–N bond.[202,203]

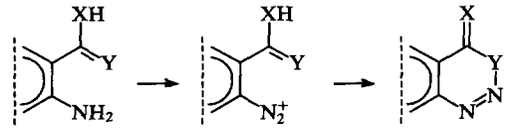
These results have been explained[203] by the existence of an acid–base equilibrium between the diazo-compounds **135** and **136**, each of which gives rise to its own cyclisation product — compounds **137** and **138** respectively.



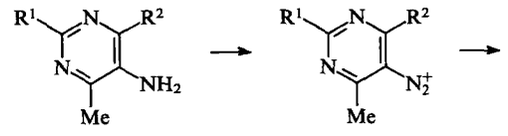
R = COMe, CO_2Et, H.

b. The formation of N–N and N–S bonds

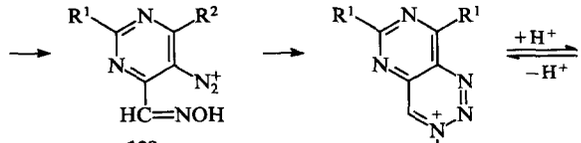
The diazotisation of heterocyclic and aromatic amines containing amide, amidine, and thioamide groups in the *ortho*-positions takes place via intermediate diazo-compounds with formation of condensed 1,2,3-triazines and thiadiazines.



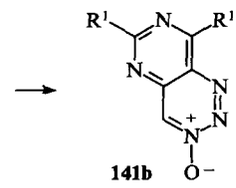
X, Y = O, S, NR.



140



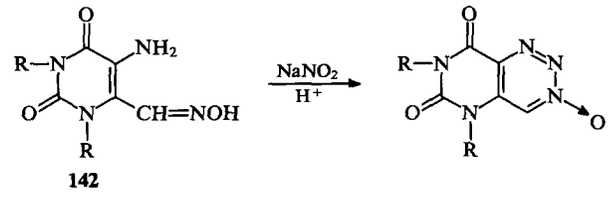
139 **141a**



141b

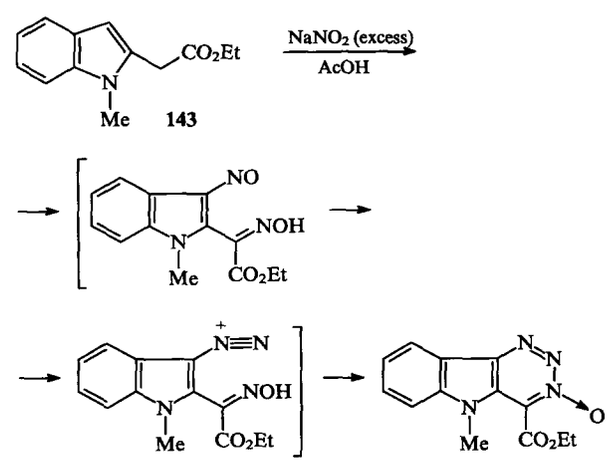
Thus the diazooximes **139**, formed from the amines **140** as a result of diazotisation and nitrosation reactions, cyclise to pyrimido[4,5-*d*]-1,2,3-triazines **141**.[196,204]

The interaction of the amines **142**[196] and indoles **143**[205] with nitrous acid affords analogous results.



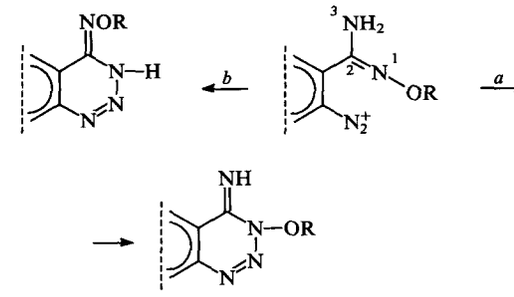
142

R = H, Alk.



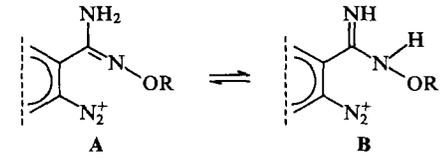
Diazo-compounds containing an amidinoxime group can cyclise, in principle via two paths — with participation of the N(1) and N(3) atoms.

However, it has been shown[196,206] that this reaction involves the formation of a N–N bond with the N(1) atom linked to the oxygen atom (route *a*).



R = H, Alk.

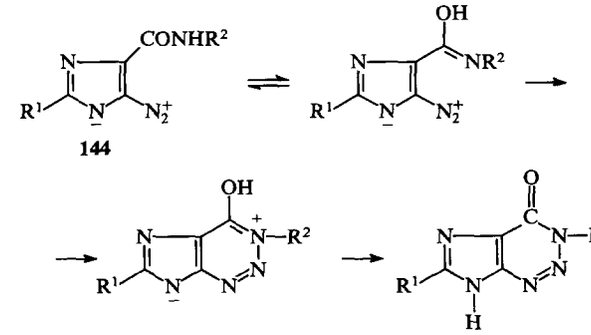
The higher reactivity of the nitrogen atom linked to the oxygen atom can be accounted for either by the α-effect of the lone pair of the oxygen atom or by the existence of amidinoximes fully in the tautomeric form **A** and by the high energy barrier to the conversion of form **A** into form **B**.



A **B**

R = H, Alk.

Data indicating a higher reactivity of the amide nitrogen atom linked to the heteroatom with a lone pair are confirmed by the series of studies of Mokyushin and coworkers[192–195] on the cyclisation of heterocyclic diazo-compounds containing an amide¶, hydroxyamide, and hydrazide group in the *ortho*-positions.[207–210] The authors showed that, despite their tendency to cyclise, the diazo-compounds **144** (R^2 = H, Alk, Ar) may be isolated and characterised spectroscopically. However, this does not apply to compounds **144** with R^2 = OH, NH_2, or N=CHAr.



144

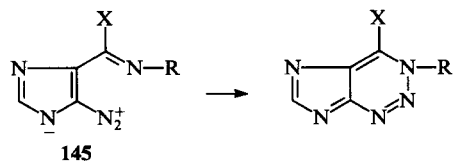
R^1 = H, SMe, SAr, SHet, SH, Ph;

R^2 = H, Alk, Ph, OH, NH_2, NCH_2Ar.

They cyclise already during their synthesis, which indicates their higher reactivity compared with other representatives of this series.

¶ The cyclisation of diazo-compounds with the *o*-amide group as a method of synthesis of condensed triazinones has been described in numerous publications.[207–215]

The heterocyclic diazo-compounds **145**, containing the amidine and imidate groups, also cyclise to triazines under the conditions of the synthesis.[196]

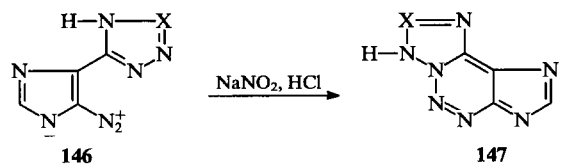


145

X = OAlk, NH_2, SMe.

Nevertheless, Mokrushin and coworkers[216] were able to isolate and characterise spectroscopically the diazo-compounds **145** (X = SMe).

The cyclisation of the diazo-compounds **146**, in which the amidine group is represented by a triazole or tetrazole ring, leads to the formation of the tricyclic compounds **147**.[217-219]

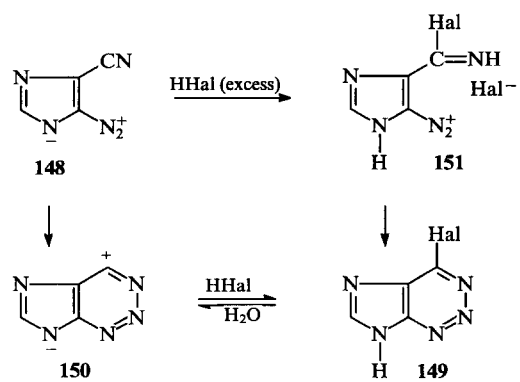


146 **147**

X = CH, N.

The diazo-compounds **148**, containing a cyano-group in the *ortho*-position, are converted into the imidazotriazines **149** on treatment with hydrogen chloride or bromide.[220,221] In aqueous media, the reaction proceeds in the opposite direction.

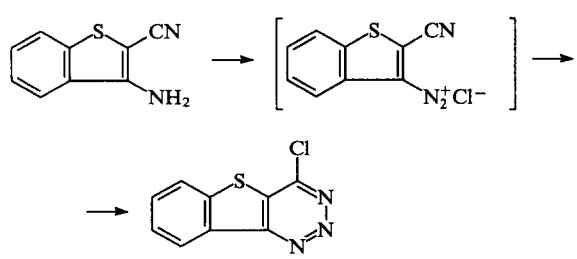
The authors[220,221] suggested that this reaction is achieved via the intermediate compound **150**. However, in our view, the mechanism involving the diazoimine **151** as an intermediate is more probable.



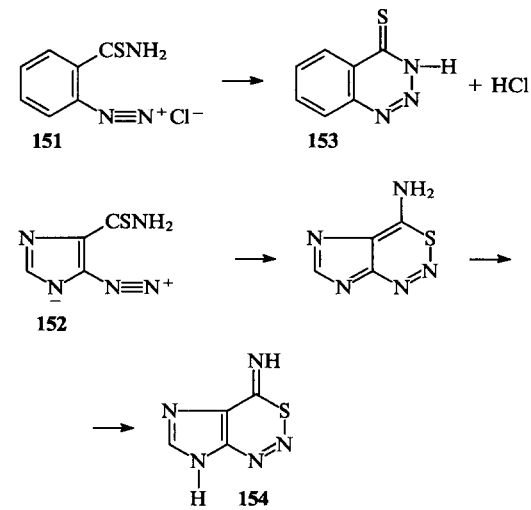
148 **151** **150** **149**

Hal = Cl, Br.

Beck and Yahner observed a similar reaction but in other systems.[222]



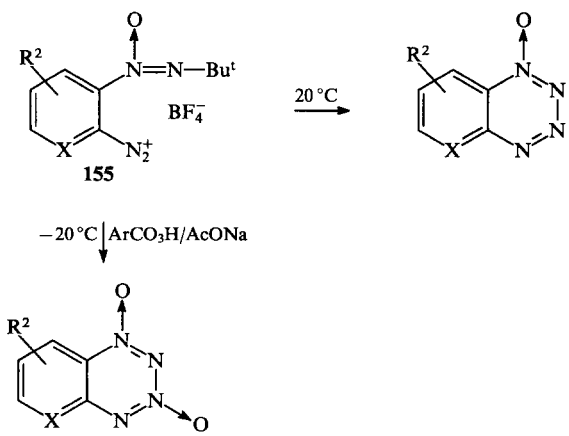
It is of interest to note that the cyclisation of the aromatic diazonium salts **151** and of the heterocyclic diazo-compounds **152**, containing a thiocarbamoyl group in the molecule, takes place via different paths with formation of 1,2,3-triazinethiones **153**[223,224] and thiadiazines **154**.[225,226]



151 **153** **152** **154**

It is not understood whether this is associated with the different reactivities of the diazo- and diazonium groups or with the different thermodynamic stabilities of the imidazo- and benzo-thiadiazines.

The cyclisation of the diazonium salts **155**, containing an azoxy-group in the *ortho*-position, leads to the *N*-oxides of heterocycles with four nitrogen atoms — tetrazines.[227,228]



155

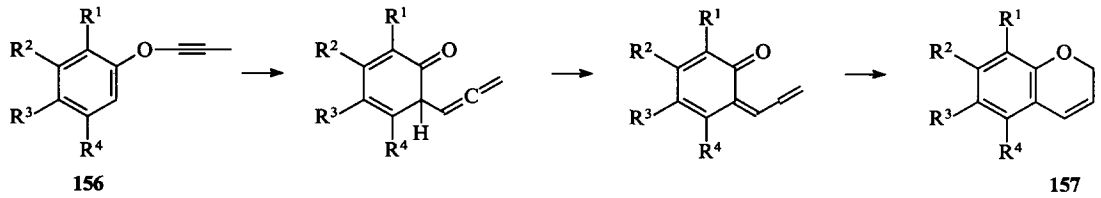
3. Reactions of oxygen-containing compounds

a. Compounds with one oxygen atom

The 1,6-ER of dienones to pyrans, which is extremely interesting from the standpoint of theoretical studies and practical use, belongs to processes of this type. It constitutes the basis of the manifestation of the photochromic and thermochromic properties by spiropyrans,[229] chromenes,[230,231] and spirooxazines[232] and is one of the stages in a wide variety of chemical transformations of, for example, the propargyl ethers **156** into the benzopyrans **157**,[4] of the pyrylium salts **158** into the pyridinium salts **159**[233,234] (on treatment with aliphatic and aromatic amines), of compounds **160** into the benzene derivatives **161** (on treatment with phosphoranes[235] and enamines[236]), and also of the isoxazolium salts **162** into the 1,3-oxazines **163**[237] (Scheme 7).

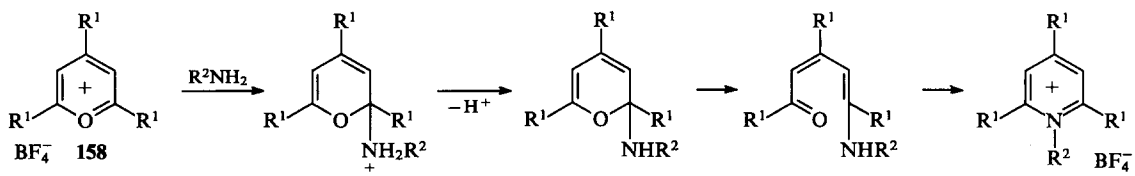
It has been shown that, on heating with diethyl ethynedicarboxylate, the dithioacetal **164** gives rise to the thiapyranone **165**. This illustrates a series of consecutive pericyclic reactions: cycloaddition (CP), 1,4- and 1,6-ER and sigmatropic rearrangements (Scheme 8).[238]

Scheme 7



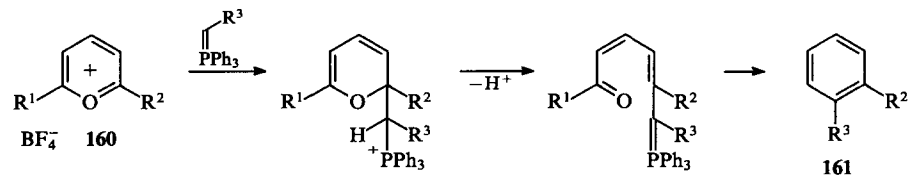
156 **157**

R^1, R^2, R^3, R^4 = H, Me, Cl, OMe.



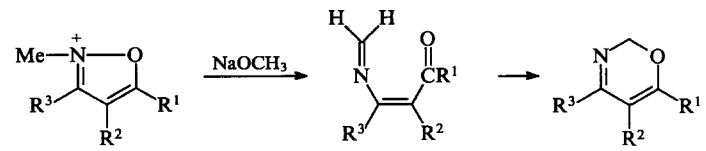
158 **159**

R^1 = Ph, 4-FC_6H_4; R^2 = Bu, Bz, C_6H_{11}, Ph.



160 **161**

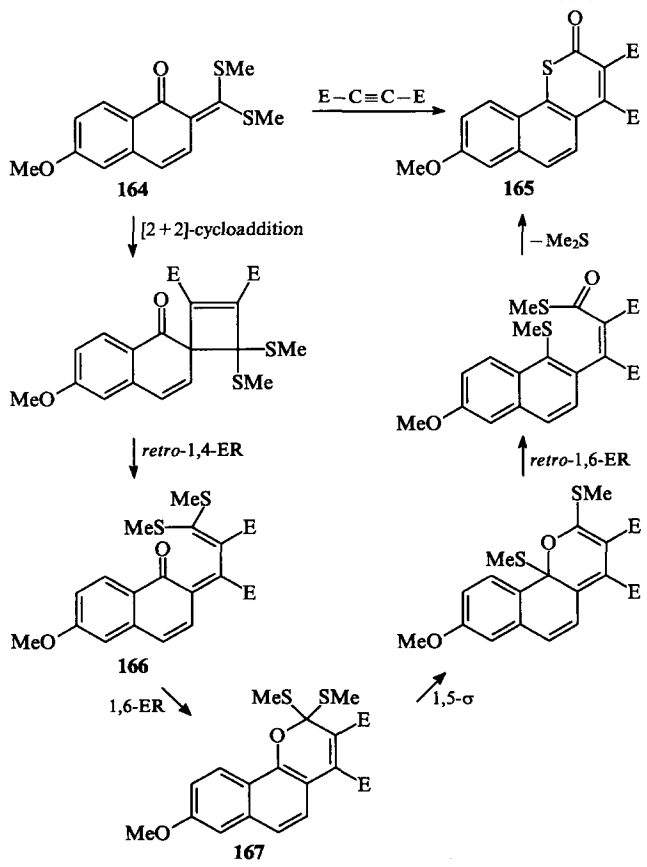
R^1, R^2 = Me, OMe; R^3 = CO_2Et.



162 **163**

R^1, R^2, R^3 = H, Ph.

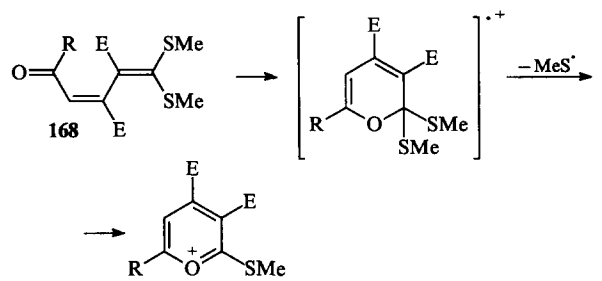
Scheme 8



164 **165** **166** **167**

E = CO_2Et.

It has been shown[238] that the 1,6-ER of compound **166** to compound **167** is analogous to the mass-spectrometric decomposition of compound **168**.

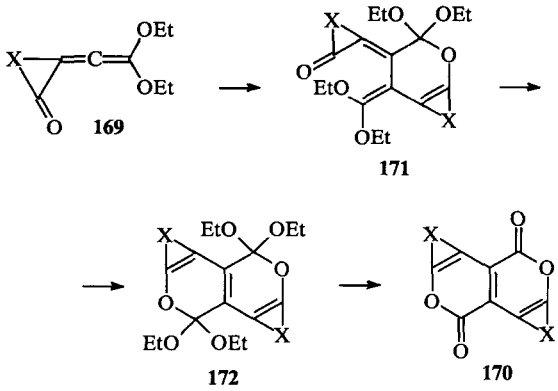


168

E = CO_2Et.

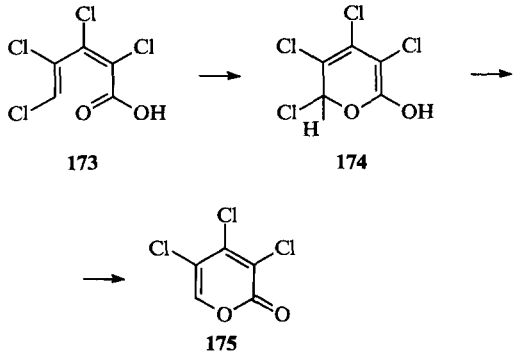
Saalfrank et al.[239] showed that compound **169**, which is stable at moderate temperatures, gives rise to the pyranone **170** on thermolysis, probably as a result of the consecutive [4 + 2]-cycloaddition and 1,6-ER reactions of the intermediate dienone **171** and the hydrolysis of the diacetal **172**.

The cyclisation of the polyhalodienone **173** does not stop at the ER stage. The 2*H*-pyran **174** formed is stabilised as a result of the elimination of a hydrogen halide molecule and is converted into the pyran-2-one **175**.[240,241]



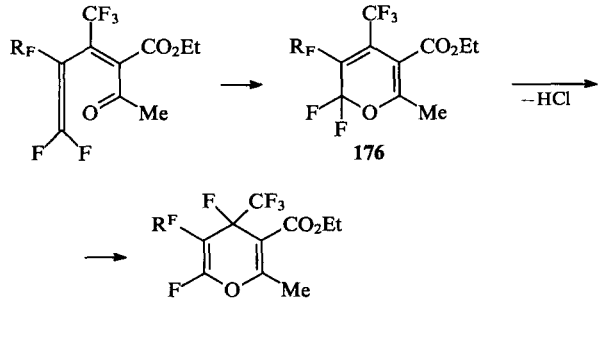
169 171 172 170

X = $(CH{=}CH)_2$.



173 174 175

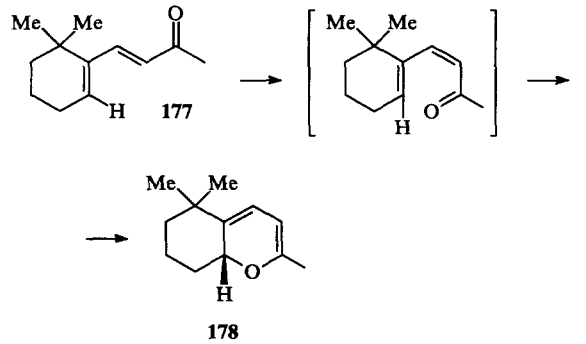
The polyfluorinated pyrans **176** are stabilised by the 1,3-sigmatropic shift of a fluorine atom.[242]



176

R_F = $(C_2F_5)_2CCF_3$, $C(CF_3)_3$, C_2F_5, F.

A study of the products of the irradiation of the *trans*-dienone **177** (to which the structure of the pyran **178** had been initially attributed) by ^{1}H NMR spectroscopy showed that at 55 °C the products consist of 18.8% of the dienone **177** and of 82.2% of the 2*H*-pyran **178**.[4]

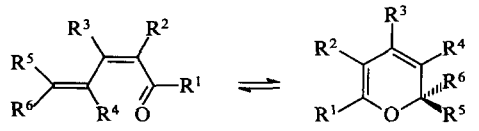


177 178

It has been shown that the ring closure in *cis*-β-ionone is a rapid unimolecular reaction which is relatively insensitive to the solvent.[4] The enthalpy and entropy of activation for this process are 20 kcal mol^{-1} and −5 entropy units, whereas the corresponding quantities for the cyclisation of *cis,cis*-1-cyclohexenylpenta-1,3-diene are 34 kcal mol^{-1} and −5 entropy units respectively. Thus the substitution of the terminal methylene group by an oxygen atom lowers the activation energy by 14 kcal mol^{-1}. Several causes accounting for this phenomenon have been put forward in Marvell's book.[4]

The available literature data did not permit conclusions concerning the influence of the electron-donating and electron-accepting properties of the substituents on the rate of this 1,6-ER.

According to Benson's data,[4] the difference between the enthalpies of formation of *cis*-pentadienes and α-pyrans is −0.1 kcal mol^{-1}. In the absence of other strong interactions, the equilibrium between the dienones and pyrans is therefore determined by entropy factors.



179 180

R^1–R^6 = H, Alk, OAlk, NHAlk, COOAlk, COAlk, CN, Ar.

A systematic and detailed study of the influence of the structure on the equilibrium between dienones and the isomeric 2*H*-pyrans has been carried out by Krasnaya and co-workers.[243–248] They showed that the intensification of the steric interactions between the substituents in the α- and γ-positions as well as the introduction of a dimethylamino-group in the β-position displace the equilibrium towards the pyran form, whereas an increase in the capacity of the solvent for specific solvation entails an increase in the fraction of the diene form. Among compounds **179** (R^4 = Br, OEt), containing bromine or the ethoxy-group, solvatochromism is most pronounced. In hexane or tetrachloroethene, they exist in the form of 2*H*-pyrans, whilst in water or in a water–methanol mixture they are present as the dienones.

It is of interest to note that the content of valence isomers may depend on the state of aggregation of the given substance. Thus compound **179** [R^1, R^2 = $-(CH_2)_4-$, R^4 = OEt] exists in the crystalline state as the dienone **179**, whilst in solution or in the melt it is present as two isomers — the dienone **179** and the pyran **180**.

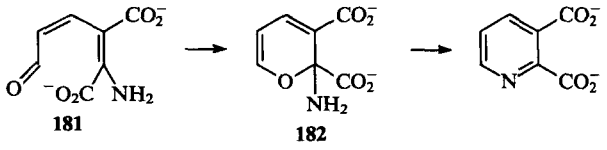
The authors[242–249] explain their findings by the fact that, with increase in the steric hindrance between the substituents R^5 and R^3 and also between R^4 and CO, the equilibrium shifts towards *cis*-form of the dienone, which is favourable for cyclisation. Their explanations are similar to those used by Duperrier and Dreux,[250] who showed that the steric interaction between R^3 and R^5 and also between R^4 and CO can be important for the cyclisation reactions, while the groups R^4 and R^6, conjugated with the π-system, displace the equilibrium towards the dienone.

In connection with the manifestation of photochromic properties by chromenes and spiropyrans, a series of theoretical and experimental studies have been carried out on the photochemical reactions of these compounds.[251–260] It has been shown[258] that $^1(\pi\pi^*)$ singlet state of the spiropyran is decisive in this process but that in the photochemical reaction a crossing of the type $^1(\pi\pi^*)-{}^3(n\pi^*)$ or $^1(n\pi^*)-{}^3(\pi\pi^*)$ takes place.

However, Khlomanskii and Dyumaev[259] believe that these processes do not fully account for the nature of the primary photochemical step in spiropyrans.

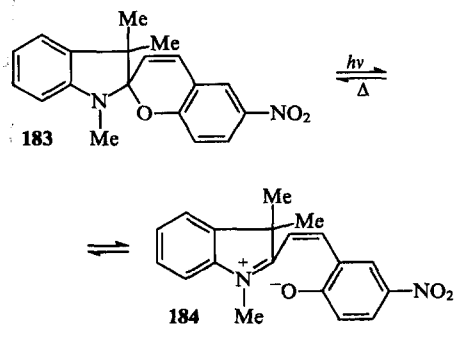
The rapid reactions of dienones and 2*H*-pyrans are the cause of the ready isomerisation of retinal relative to the double bonds.[261,262] It has been shown that pyrans are reduced via the dienones initially formed.[263,264]

In connection with the high sensitivity of the equilibrium between dienones and 2*H*-pyrans to the influence of the pH of the medium, temperature, and irradiation by light, it has been suggested[18] that this ER plays an important role in biochemical processes in living organisms. The study by Keys and Hamilton[265] constitutes a confirmation of this hypothesis. It was shown in the latter that one of the key stages in the biosynthesis of pyridine-2,3-dicarboxylate in animals is the cyclisation of 2-amino-β-carboxymuconate ε-semialdehyde **181** to the pyran **182**.



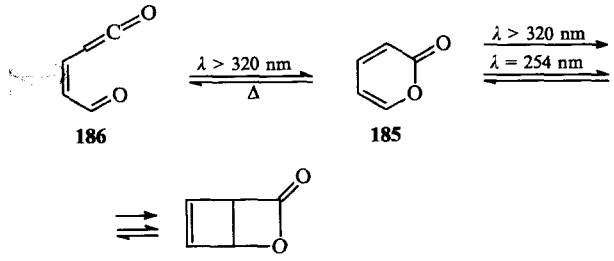
181 **182**

In this connection, one should also note that the system **183**↔**184** functions as an agent transferring aminoacids through liposomes.[266]



183 **184**

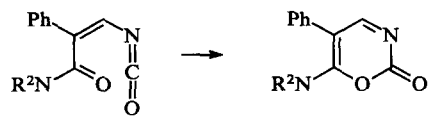
The replacement of the terminal double bond by the ketene group in the dienone leads to the displacement of the equilibrium towards the cyclic form.[4] The low-temperature photolysis of the pyranone **185** makes it possible to identify the ketene **186**, which is converted irreversibly into the initial compound after the cessation of UV irradiation.[267–269]



186 **185**

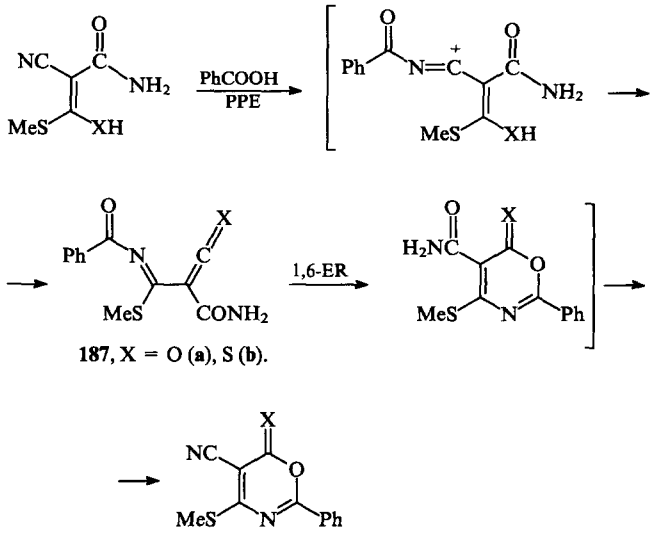
This fact made it possible to carry out a kinetic study of the cyclisation of the ketene **186**. The activation energy for the ketene is 9.4 kcal mol^{-1} and its lifetime at 26.5 °C is only 2.4 μs.

Isocyanates containing the 2-azadienone system also readily cyclise to oxazinones.[270–272]



R = Alk, R_2N — .

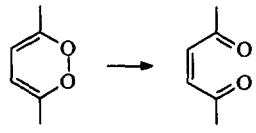
It has been shown that the 1,6-ER of the aza-analogues of compound **186** — the ketenes **187a** and the thioketenes **187b** — is one of the stages in the double O,N- and N,N-rearrangements.[273,274]



187, X = O (**a**), S (**b**).

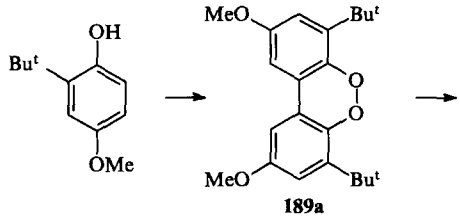
b. Compounds with two oxygen atoms

The reaction involving the opening of the ring in the potential 1,2-dioxine **188** should have a low activation energy and should be largely exothermic according to Marvell.[4]

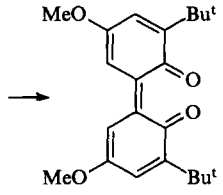


188

Nevertheless, Baltes and Volbert[275] were able to obtain its derivative — the dioxine **189a** — by oxidising 2-*tert*-butyl-4-methoxyphenol. The colourless compound **189a** acquires a deep blue colour on dissolution in nonpolar solvents, apparently as a result of its conversion into the diketone **189b**.



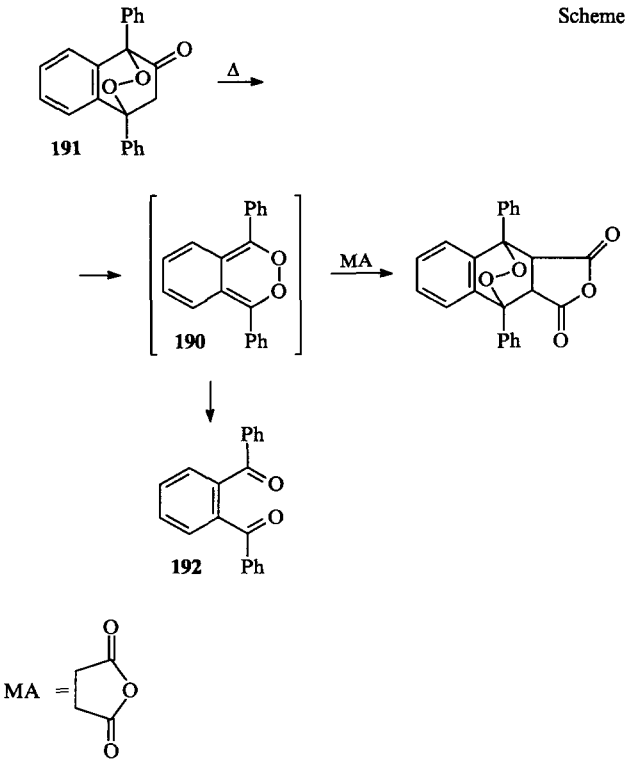
189a



189b

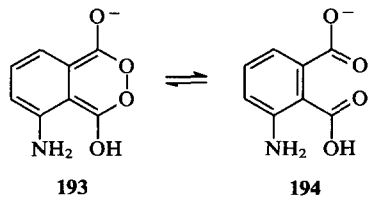
Proof of the existence of *o*-xylylene peroxide **190** as an intermediate in the decomposition of compound **191** was obtained chemically in its reaction with maleic anhydride (MA). In the absence of MA, electrocyclic opening of the dioxine ring and the formation of *o*-dibenzoylbenzene **192** take place (Scheme 9).[276]

Scheme 9



Chemiluminescence is observed during the formation of compound **192**, which indicates its existence in an excited state.

In a discussion of the chemiluminescence, Michl[277] suggested that the endoperoxide **193** is a direct precursor of the luminescent phthalate ion **194** and put forward qualitative arguments explaining why the dissociation of the O–O bond leads to chemical excitation.



Michl's model is most clearly illustrated by a qualitative correlation MO diagram (Fig. 2).

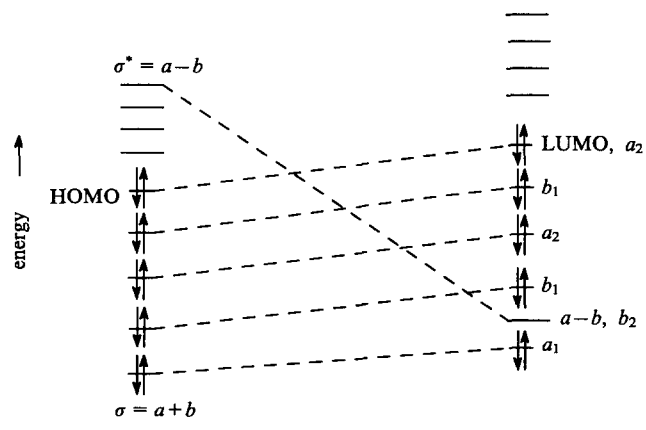
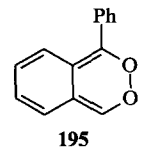


Figure 2. Qualitative correlation diagram for the MO of compounds **193** and **194**.

In the endoperoxide **193**, $a + b$ is a bonding orbital and $a - b$ is an antibonding orbital. With increase in the O–O distance, the energies of the two orbitals approach one another. In a rapid nonadiabatic reaction, the electrons do not have sufficient time to pass to an orbital with a different symmetry. This entails the failure to fill the $a - b$ orbital, whereas the LUMO becomes doubly occupied, i.e. we arrive at a doubly excited state, the transition from which to the ground state is accompanied by chemiluminescence.

Michl's qualitative model has been developed and refined by means of quantum-chemical calculations in terms of the HAM (Hydrogen Atom in Molecule) approximation.[160]

The authors[160] showed that two intersections on the correlation MO diagrams are important for the manifestation of the phenomenon of chemiluminescence. The activation energy for the opening of the endoperoxide ring in compound **193** is only 6 kcal mol^{-1}. Schuster and coworkers[278] demonstrated the unexpected stability of the *o*-xylylene peroxide **195**.

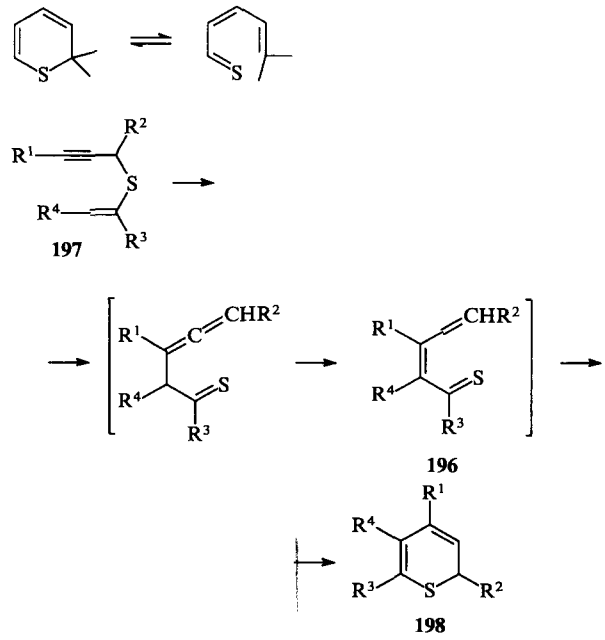


Calculations in terms of the HAM approximation explain such behaviour in the following way: the replacement of the phenyl group by an OH group increases the energy of the HOMO and lowers that of the LUMO, which diminishes the energy gap and promotes the nonadiabatic transition, lowering thereby the activation energy for the ring opening process.[160]

On the basis of calculations for the conversion of butene-1,4-dione into 1,2-dioxacyclohexadiene in terms of the MINDO/3 approximation, Pichko[138] concluded that cyclisation of this compound has a 'disrotatory' mechanism.

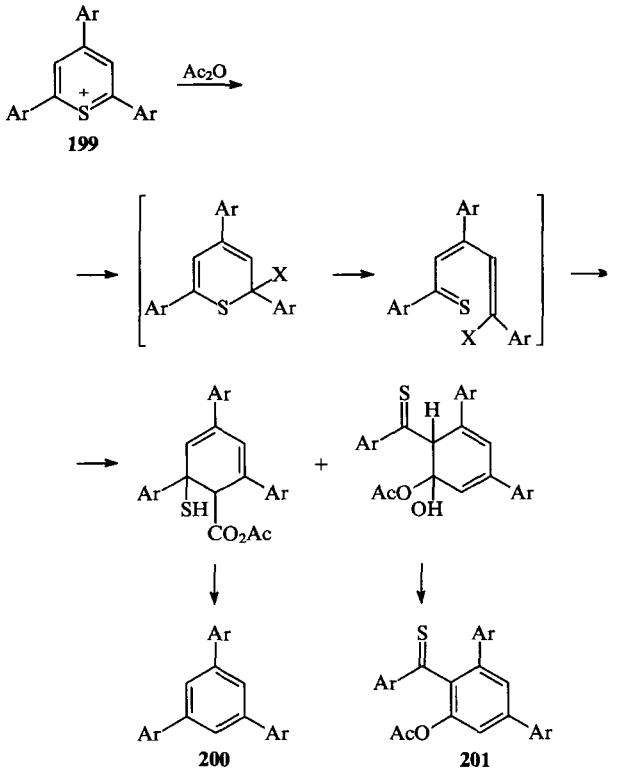
4. Reactions of sulfur-containing compounds

It has been shown by MINDO/3 calculations that thiopyrans are much more stable than their open-chain isomers.[254] Experimental data are fully consistent with the calculated results. Thus, the 1-thiahexatriene **196**, formed from the sulfide **197**, cyclises to the thiopyran **198** under the conditions of its synthesis.[4]



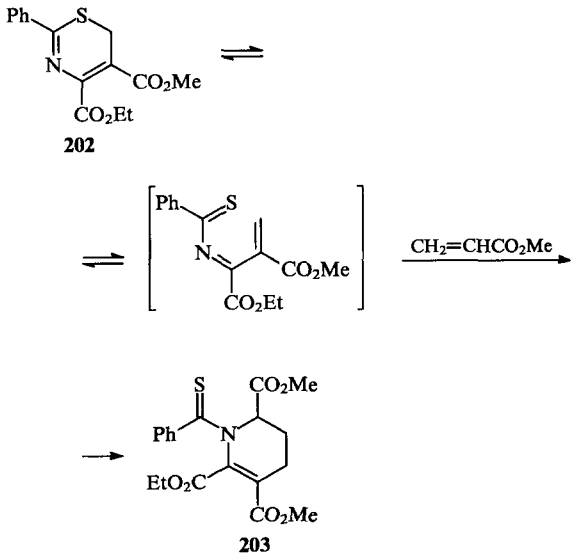
R^1, R^2, R^3, R^4 = Me, Et.

Nevertheless, the transformations of the thiopyrylium salts **199** into compounds **200** and **201** on treatment with acetic anhydride, described by Zimmermann and Fischer,[279] and of the thiazine **202** into the pyridine **203** in the presence of a dienophile[280] confirmed the possibility of the electrocyclic opening of the thiopyran ring.

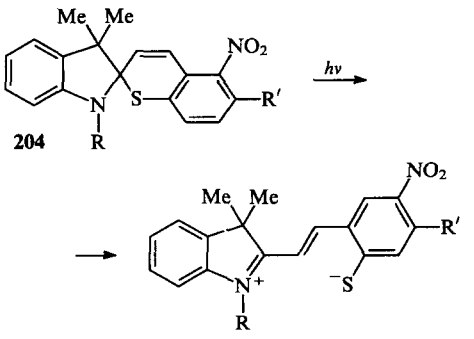


X = CH_2COOAc.

Ar = RC_6H_4, R = Ph, 4-Me, 4-MeO, 4-Cl, 4-Br.



Data concerning the manifestation of photochromic properties by the spirothiopyrans **204** — structural analogues of the spiropyrans **183** — have been published.[281] The authors[281] suggest that the photochromism of these compounds is associated with the electrocyclic opening of the thiopyran ring.

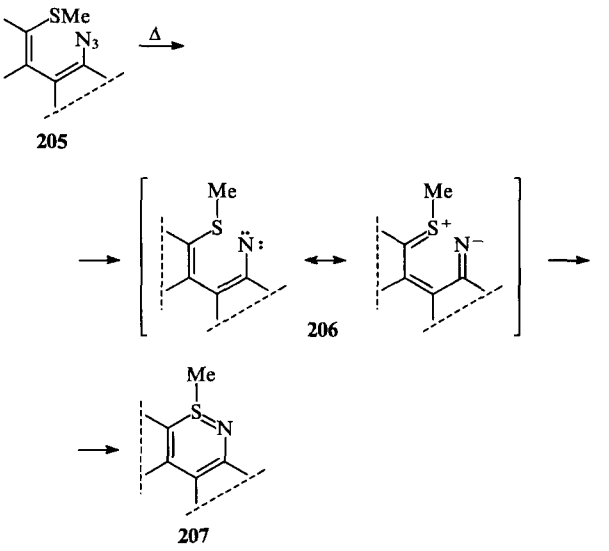


R = Me, Pr^i, $C_{18}H_{37}$,

R′ = $CH_2O_2CCMe{=}CH_2$, $CH_2OC(CH_2)_{20}Me$.

Theoretical and experimental studies[282] have demonstrated that, like thiopyrans, 1,2-dithiines are more stable than the isomeric 1,6-dithiahexatrienes.

The thermolysis of aryl, heteroaryl, and vinyl azides **205**, containing the thioether group, entails the initial formation of the nitrenes **206**, which then cyclise to the thiazines **207**.[283]



Compounds **206** may cyclise via the electrocyclic mechanism or as a result of the interaction of the lone pair of the nitrogen atom and the unoccupied orbital localised on the nitrogen atom, i.e. the heteroelectrocyclic mechanism.[5] Unfortunately, there have been no theoretical studies on this reaction.

* * *

Together with the striking advances in the application of 1,6-electrocyclic reactions in the synthesis of a whole series of different substances of practical importance and its application to achieve an understanding of the processes occurring in living nature, there have been only a few publications dealing with the study of the details of the mechanism of the 1,6-ER by computational methods.

So far it is not clear what causes the low activation energy in the reactions of hexa-1,3,5-trienes the double bond of which forms part of allene and heteroallene groups and the anomalous stability of the heteroanalogues of norcaradiene. The role of the π-system in the cyclisation of aromatic diazonium salts containing vinyl and azomethine groups in the *ortho*-position has not been discovered.

There is no doubt that the solution of these problems will lead to a fuller understanding of the characteristics of electrocyclic reactions.

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